LIST OF PLATES

CHAPTER I

MEAT AND ITS PREPARATIONS

MEAT

In its ordinary meaning, the term meat is applied to parts of slaughtered animals consisting principally of muscular tissue together with larger or smaller quantities of tendons, adipose tissue, bone, etc.

The examination of meat concerns in the first place the food inspector, whose duty it is to determine that the meat is good for food and has not been obtained from diseased animals. The analyst's task is usually to determine the nutritive value of the meat by estimating its principal components and to test for the presence of preservatives or colouring matters. The more common chemical tests and determinations are as follows:

Sampling.—About 500 grams are required, and this quantity is usually taken from several (3–5) of the more fleshy parts of the carcase. The pieces are freed from bone, cut into pieces a few grams in weight by means of a knife and then converted in a mincing machine into a fine pasty mass, which is well mixed so as to give a homogeneous sample.

1. External and Objective Characters.—Observations are made of: the colour (whether bright red or brownish-red), the consistency (whether compact and elastic or the reverse), and the odour (whether normal and not unpleasant, or, on the other hand, indicative of putrefaction). Note is also made of the odour and taste of the broth obtained by boiling a piece of the meat with water in a closed vessel—the odour at the moment the liquid begins to boil. Observation is also made of the reaction—whether this is amphoteric, or acid, or alkaline; the last indicates putrefaction.

2. Determination of the Water.—About 10 grams of the prepared sample are weighed exactly in a flat porcelain dish, the fragments being spread over the whole surface of the dish, which is left in a steam-oven for about four hours and then transferred to an air-oven at 105°. After a further two hours the dish is cooled and weighed and then heated for about another hour, after which the weight is usually found to be unchanged.

The moisture in meat may also be calculated by subtracting from 100 the sum of the percentages of fat, albuminoids and ash.

3. Fat.—This may be determined on the dry residue from 2, which is placed in a filter-paper thimble in an extraction apparatus, while the dish is rinsed out with anhydrous ether or light petroleum into the extraction flask. The extraction is continued for about six hours, after which the bulk of the solvent is distilled off on a water-bath, while the remaining

liquid is then evaporated at a gentle heat in a tared glass dish and the residual fat dried for two hours in a steam-oven, cooled and weighed.

4. Nitrogenous Substances.—These are determined by Kjeldahl's method, as follows :

About 0·7–0·9 gram of the dried and defatted or only dried meat is gradually heated to boiling in a Kjeldahl flask with 10 c.c. of concentrated sulphuric acid and about 0·5 gram of copper oxide, the boiling being continued until the substance is completely attacked, this requiring about two hours. Finely powdered potassium permanganate is then added to the hot liquid until the latter assumes a greenish-brown tint. The cold liquid is diluted with water, placed in a distillation flask, treated with 40 c.c. of 50% caustic soda solution, and about 100 c.c. distilled over into 15 c.c. of semi-normal sulphuric acid (*see* Fertilisers, Vol. I, p. 122). The excess of acid is titrated with N/2-alkali in presence of methyl orange : 1 c.c. N/2-sulphuric acid = 0·00702 gram of nitrogen, and 1 gram of nitrogen = 6·25 grams of albuminous matters.

The latter calculation, based on the supposition that all nitrogenous substances of animal origin contain 16% of nitrogen, is not quite exact, but it gives results which are usually satisfactory and are very near to the percentages of nitrogenous compounds calculated by difference : the sum of the moisture, fat and ash being deducted from 100.

5. Ash.—In a fairly large platinum dish a weighed amount (about 10 grams) of the meat is carefully charred, the carbonaceous mass being twice triturated with a small, clean pestle. When charring is complete, the mass is treated several times in the dish with small quantities of hot water, which are then poured on to a small filter. The residue on the filter is washed well with a little water and the filter and its contents placed in the platinum dish, dried and completely incinerated. To the ash thus obtained is added the liquid from the lixiviation of the carbon, the whole being evaporated to dryness on the water-bath and the residue gently ignited, cooled and weighed.

The *qualitative analysis* of the ash is carried out as usual.

When a *quantitative determination of the phosphoric acid and chlorine* is required, a fresh quantity of ash is prepared from a weighed amount of the meat sample mixed with an alkali such as milk of lime, sodium carbonate, etc. The phosphoric acid and the chlorine are determined in the nitric acid solution of the ash, the former by the ammonium molybdate method, and the latter either volumetrically or gravimetrically as silver chloride.

6. Detection and Estimation of Preservatives.—The antiseptics commonly tested for in meat are formaldehyde, formic acid, boric acid and fluorides. The analytical methods used for the detection of these and other antiseptics are given later (*see* Sausages).

7. Colouring Matters.—50 grams of the meat are well shaken in a beaker with a solution of sodium salicylate in aqueous glycerine (5 grams of the salicylate in 100 c.c. of a mixture of water and glycerol in equal volumes), the beaker being heated on a steam-bath for half an hour. The cold mass is filtered through linen and the solid matter pressed, the liquid being then filtered through paper until clear.

If the filtrate is yellowish and not reddish, the absence of colouring matter is at once concluded. With a reddish filtrate, about one-third of this is treated in a cylinder with a few drops of alum solution and then slight excess of ammonia : if after a rest of some hours the precipitate is red, the presence of carmine is indicated.

With the remainder of the liquid, mixed with 10 c.c. of 10% potassium bisulphate solution and a few drops of acetic acid, two or three strands of well-defatted wool are heated on a water-bath for a long time. In presence of coal-tar dyes, the wool is coloured red, the colour persisting after washing with water.

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Meat, as defined above, varies widely in composition, not merely with the individual animal yielding it, but also according to the breed, age, etc., of the animal, to the part of the body from which it is obtained, and to the method of slaughtering employed. The *total nitrogenous substances* are mostly about 20%, and the *fat* and *water* vary together, the one increasing as the other diminishes ; for instance, fat beef with 32·50% of water may contain 55·1% of fat, while lean meat with 74·20% of water may contain only 3·45% of fat.

The ash amounts to almost 2% and contains mainly potassium phosphate, with less proportions of calcium and magnesium phosphates and sodium chloride.

Freezing does not appreciably modify the composition of meat ; it causes the loss of a little water (not much more than 1%) but no change in the nitrogenous substances and fat.

SAUSAGES

The objects of chemical analysis are the same with sausages as with fresh meat, and the various determinations are made in the same way. For detecting certain special adulterations the following methods are used :

1. External and Objective Characters.—The appearance, odour and taste of the meat are compared with those of the corresponding fresh meat, note being taken of the retention or otherwise of the more or less deep red colour of the muscular parts ; the fat is observed to ascertain if it is white and of pleasant odour, and the mass of the meat to see if it is compact and without empty spaces and not excessively moist.

Any mould completely or partially covering the surface is noted. When such is present, the interior often contains somewhat soft masses of rancid, bitter taste and disagreeable odour which, when cut, reveal lean parts of a grey or greenish colour and fat coloured yellow or greenish. These indications denote fairly advanced putrefaction ; often, however, the signs of putrefaction in its initial stages are apparent to a less degree or not at all, and in such cases the changes are detectable only by bacteriological examination.

2. Water.—This is determined as in fresh meat (2, above).

Sausage meat is not infrequently rich in water, which is added fraudulently ; water is also added with starch paste and in such a case this determination is of special importance.

3. Determination of the Acidity of the Fat.[1]—From 5 to 8 grams of

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[1] Schweiz: *Wochenschrift f. Chem. u. Pharm.*, 1910, XLVIII, p. 481.

the finely minced mass are mixed with well washed sand and treated with ether, the ethereal solution of the fat being filtered and made up to 50 c.c. ; 5 c.c. are evaporated in a tared glass dish and the residue dried for 45 minutes in a steam-oven and weighed. The remaining 45 c.c. are mixed with 45 c.c. of 45% alcohol and the acidity then titrated with N/10-caustic soda in presence of phenolphthalein. If a represents the weight of the dried residue from 5 c.c. of the ethereal solution and b the number of c.c. of alkali used in the titration, the degree of acidity of the fat expressed in normal alkali is given by the formula,

$$A = \frac{10b}{9a}.$$

4. Detection of Albumin (Casein, Egg Albumin).—Albumins may be added to render the meat paste more dense and compact. They may be detected as follows :

(a) According to Feder,[1] the presence of *casein* is shown by a high proportion of lime in the ash, defatted meat containing only 0·06–0·13% of lime, whilst casein contains about 2%. 10 grams of the sample are carefully defatted, the residue being incinerated and the ash dissolved in dilute hydrochloric acid ; the acid liquid is treated with ferric chloride and sodium acetate to eliminate the phosphoric acid, and then heated until all the precipitate is thrown down, boiled and filtered. In the filtrate the lime is determined by means of ammonium oxalate in the usual way.

(b) *Albumin* may be detected by the marked alkalinity of the ash, since commercial albumins mostly contain alkali. Thus, while the alkalinity of 100 grams of dry pork is 8·1 c.c. of normal acid, the addition of 1% of commercial albumin increases it to 20 c.c.

5. Detection and Determination of Starch.—(a) *Qualitative test.* A freshly-cut surface of the sample is treated with a few drops of iodine solution to see if a blue coloration is formed. If the result of this test is doubtful, a quantity of the dry, defatted substance is triturated well with a little water, and after depositing for a short time, the turbid liquid examined under the microscope. A little iodine solution is then added and the specimen again examined microscopically for stained starch granules.

(b) *Quantitative determination.*[2] 10 or 20 grams of the sample, according to the intensity of the iodine reaction, are heated on the waterbath in a covered beaker with 50 c.c. of 8% alcoholic potash solution, the liquid being frequently stirred. As soon as the mass is dissolved, the liquid is diluted with 2–3 volumes of hot 50% alcohol and, after standing for some time, filtered through a Gooch crucible containing asbestos.

The contents of the crucible are washed twice with hot 8% alcoholic potash and then with 50% alcohol until the filtrate ceases to give an alkaline reaction and remains clear on addition of acetic acid ; the washed precipitate is heated for about half an hour in the original beaker on a water-bath with 60 c.c. of 6% aqueous potassium hydroxide, with frequent stirring. The cold liquid is made up to 200 c.c., allowed to settle thoroughly, and 50 c.c. of it acidified in a beaker with acetic acid and treated with an equal

[1] *Zeitschr. Unt. Nahr- und Genuss-mittel*, 1909, XVII, p. 191.
[2] Mayrhofer ; *Forschungsber.*, III, 1896, pp. 141, 429.

volume of 96% alcohol, which precipitates all the starch. The precipitate is collected in a tared Gooch crucible and washed thoroughly with 50% alcohol, then with absolute alcohol and finally with ether.

The crucible is dried first at 40° and then at 100° to constant weight, being subsequently calcined, cooled and again weighed; the difference between the two weights gives the starch free from ash and water. To express this value as potato starch, etc. (which is what is usually added), it is divided by 0·8; to express it as cereal flour, it is divided by 0·67.

This method precipitates also the small quantity of glycogen in the meat; as a rule this does not influence the results appreciably, but when the separation of starch from glycogen is necessary, especially in presence of horseflesh, Mayrhofer's modified method is used (*see* later).

It should also be noted that part of the starch found may be derived from the spices used, this being allowed for by subtracting 0·5% of the quantity found.

6. Detection of Horseflesh.—The methods here used are based on the detection and determination of the glycogen and on an examination of the fat.

A. DETECTION AND DETERMINATION OF THE GLYCOGEN:

1. *Qualitative test.* Two cases present themselves:

(*a*) *Absence of starch*: about 50 grams of the sample are subjected to prolonged boiling with 200 c.c. of water. When cold, the liquid is decanted off, treated with dilute nitric acid to precipitate the albuminoids and filtered. A little of the filtrate is treated in a test-tube with a few drops of a very dilute solution of iodine in potassium iodide; in presence of glycogen the liquid assumes a bright red colour, which disappears at 80–90° and reappears on cooling.

Feeble or transitory colorations should be disregarded, since other flesh than that of the horse may contain small proportions of glycogen. The coloration should be sharp and decided and such is obtained with fresh horseflesh or with sausage containing it, if recently prepared; the glycogen gradually disappears with lapse of time and the reaction becomes continually less marked.

Further, this coloration is not characteristic of glycogen, but is shown also by certain dextrins, which behave like glycogen on heating.

(*b*) In *presence of starch*, glycogen is tested for as follows:

A portion of the sample is heated on the water-bath with 8% alcoholic potash until the fleshy mass is dissolved. The liquid is filtered off with the help of a pump and the residue on the filter washed with cold 95% alcohol and then boiled with 96% alcohol, which partially dissolves the glycogen but leaves the starch undissolved. The filtered liquid is evaporated on a water-bath, the residue taken up in a little water and the solution tested for glycogen by means of iodine.

The detection of glycogen in presence of starch is not easy, and even the above method often gives uncertain results. In such cases use is made of biological tests for horseflesh.

2. *Quantitative estimation.* The following procedure is employed [1]:

[1] Mayrhofer and Polenske: *Zeitschr. Unt. Nahr-und Genuss-mittel,* 1901, IV, p. 1101; 1907, XIII, 355.

50 grams of the sample, freed from any adherent fat, are heated in a covered beaker on a water-bath with 150 c.c. of alcoholic potash (80 grams of potassium hydroxide in a litre of 90% alcohol), the liquid being frequently stirred until the fleshy mass is dissolved.

The hot liquid is mixed with 100 c.c. of 50% alcohol, the impure glycogen being filtered off after cooling. The precipitate is washed with 30 c.c. of hot alcoholic potash and then with cold 90% alcohol until the filtrate is no longer rendered turbid by addition of a few drops of dilute hydrochloric acid : it is then heated in a 110 c.c. flask with 50 c.c. of normal potash on a water-bath for half an hour to dissolve the glycogen. When cold the liquid is acidified with concentrated acetic acid, made up to 110 c.c. with water and filtered.

To 100 c.c. of the filtrate are added 150 c.c. of absolute alcohol and after 12 hours the precipitate of pure glycogen is collected on a tared filter, washed successively with about 70% alcohol, absolute alcohol and ether, dried at 40° and finally at 100° to constant weight. The weight found, multiplied by 2·2, gives the percentage of glycogen.

The glycogen obtained should be a white, amorphous powder and its aqueous solution should have a marked white opalescence, should not reduce Fehling's solution and should give an intense burgundy-red coloration with iodine.

This method gives good results only in absence of starch.

B. EXAMINATION OF THE FAT. Horse fat differs from the fats of other animals in its index of refraction and iodine number.

1. *Index of refraction.* From 50 grams of the sample the fat is separated either by simple fusion at 100° or by boiling with water and separating the layer of fat. The latter is examined in the Zeiss butyro-refractometer at 40° (*see* Butter, Chapter II). If the index exceeds 51·5°, the presence of horseflesh is probable.

2. *Iodine number.* If the iodine number (*see* Fatty Substances, Vol. I) determined in the usual way exceeds 70, the presence of horseflesh may be concluded.

Proof of the presence of horse flesh by chemical methods based on detection and determination of glycogen and on the refractive index and iodine number of the fat cannot be certain in character ; the presence of glycogen and the constants of the fat may give useful indications, but definite proof is possible only by biological methods. With prepared meats, the detection of horseflesh presents still greater difficulties than with fresh meat, since they mostly consist of mixtures of different meats.

7. Detection and Determination of Preservatives.

(*a*) SODIUM CHLORIDE. 2 grams of the finely minced sample are intimately mixed with well-washed siliceous sand and a few c.c. of water in a porcelain dish so as to give a homogeneous paste. The whole is poured into a beaker and boiled with a little water for a few minutes to coagulate the albuminous substances—until the liquid becomes almost colourless. When cold, the mass is washed completely into a 100 c.c. flask and the volume made up to the mark. The liquid is filtered and the chlorine esti-

mated by Volhard's method (*see* Vol. I, p. 10, Potable Water) on 25 c.c. of the filtrate.

(*b*) POTASSIUM NITRATE. For the *qualitative test*, about 20 grams of the dried fleshy mass are freed from fat by treatment with ether or petroleum ether, the residue being shaken vigorously with 20–30 c.c. of very hot water and filtered. A certain amount of the filtrate is added gradually to a crystal or two of brucine and a little pure concentrated sulphuric acid in a porcelain dish : a distinct red coloration indicates nitrates.

For the *quantitative determination*, this method is carried out as follows :

Reagents. (*a*) 0·25 gram of crystallised brucine is dissolved in conc. sulphuric acid free from nitric acid, the solution being prepared in a 100 c.c. cylinder and made up to the mark with the sulphuric acid. This solution should be recently prepared.

(*b*) 0·10 gram of pure potassium nitrate is dissolved in a little water and made up to a litre.

(*c*) 5 grams of mercuric chloride are dissolved in 100 c.c. of distilled water and 100 c.c. of 2% hydrochloric acid added to the solution.

Standard solutions. Of solution (*b*), 5, 6, 7, 8, 9 and 10 c.c. are introduced into porcelain dishes together with 5, 4, 3, 2, 1 and 0 c.c. of water respectively and then, at once, 20 c.c. of solution (*a*). After being mixed for a few moments, each liquid is poured into a glass cylinder with a ground stopper, in which it is shaken with 70 c.c. of distilled water. This series of coloured solutions should be prepared as nearly as possible at the moment it is required.

Procedure. 50 grams of the sample are weighed out and boiled for 30 minutes with 200 c.c. of water. When cool, the liquid is filtered by decantation into a 500 c.c. flask and the residue treated again with two or three quantities of 100 c.c. of water, the volume being subsequently made up with distilled water in the flask.

To 50 c.c. of the turbid liquid are added 50 c.c. of solution (*c*), the mixture being filtered. 10 c.c. of the liquid thus obtained are poured into a dish and immediately treated with 20 c.c. of solution (*a*), the liquid being mixed, poured into a cylinder of similar dimensions to those used for the standard solutions and mixed with 70 c.c. of distilled water. Comparison of the coloration thus obtained with the standard colour solutions gives the amount of nitre in the liquid and consequently in the substance tested.

If the colour obtained is deeper than that of any of the standard liquids, the liquid tested must contain more than 0·001 gram of nitrate per 10 c.c. ; it should then be suitably diluted with distilled water.

This method is rapid and gives results sufficiently exact for practical purposes.

(*c*) BORIC ACID. For the *qualitative test*, 10–20 grams of the sample are incinerated in the usual way after addition of a few c.c. of 20% sodium carbonate solution. The carbon-free ash is treated with 5 c.c. of hydrochloric acid diluted to 10% and the solution poured into a test-tube, into which also the dish is washed with 15 c.c. of 95% alcohol. 15 c.c. of conc. hydrochloric acid (D 1·19) are then added and the well-cooled mixture

shaken with 0·2 c.c. of a 0·1% curcumin solution [1] and left at rest in the dark for half an hour, after which the colour of the liquid is observed. In presence of boric acid, this varies from faint brown (minimal traces of the acid) to pink or red ; in absence of boric acid the liquid remains yellow.

The *quantitative determination* is carried out colorimetrically in the same way with a weighed quantity of the sample. The coloration of the liquid is compared (as in estimating potassium nitrate) with a series of tubes in which solutions containing definite proportions of boric acid (0·1, 0·2, 0·3, etc., %) are treated with the same amounts of acid, alcohol and curcumin solution in each case.

This method is rapid and fairly exact. With products containing much salt, the latter settles at the bottom of the tube after treatment with alcohol and hydrochloric acid, but such deposit has no influence on the judging of the colours.

(*d*) FORMALDEHYDE. This may be detected by one of the two following tests :

(1) 5 grams of the sample are thoroughly shaken in a beaker with 10 c.c. of hot water, the mass being filtered through a cloth and well pressed. A granule of phenylhydrazine hydrochloride is dissolved in 5 c.c. of the filtrate and the solution then treated with three or four drops of 5% sodium nitroprusside solution and ten drops of 10% caustic soda solution. In presence of formaldehyde a more or less intense blue coloration is observed, this remaining unchanged for some time (*Rimini's reaction*).[2]

(2) 50 grams of the sample are mixed with an equal weight of 20% phosphoric acid solution and the mixture distilled until about 30 c.c. of distillate are collected. To this is added about 0·1 gram of peptone,[3] and to 10 c.c. of the liquid are then added a drop of 5% ferric chloride solution and, carefully, 10 c.c. of conc. sulphuric acid. In presence of formaldehyde a dark violet ring is formed, and, when shaken, the liquid becomes violet if the amount of formaldehyde is marked, or reddish-violet if the amount is very small.

(*e*) SULPHUR DIOXIDE AND ITS DERIVATIVES. In considerable quantity, sulphur dioxide is detectable by the smell. Otherwise it may be *detected* as follows :

About 50 grams of the sample are mixed intimately in a flask with 10 c.c. of 25% phosphoric acid. The flask is then closed with a cork, between which and the neck of the flask is placed a strip of starch-iodide paper moistened at the lower end, which is adjusted so as to be about 1 cm. from the meat. If the paper exhibits no coloration in the course of a few minutes the flask is heated in a water-bath until it attains the temperature of the

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[1] The curcumin may be prepared as follows : 30 grams of turmeric powder (*Curcuma longa*) are dried at 100° and then treated for four hours in an extraction apparatus with petroleum ether. The dry, defatted powder is then extracted in the same apparatus with 100 c.c. of benzene for 8–10 hours ; on cooling, the benzene solution deposits the curcumin as a fine, yellowish, crystalline powder.

To prepare solutions or curcumin paper, 0·10 gram of the turmeric is dissolved in 100 c.c. of 90% alcohol.

[2] *Ann. di farmacoterapia e chimica*, 1898, No. 3.

[3] Fresh milk, quite free from formaldehyde, may also be used ; in this case 30 c.c. of the milk are added to the distillate, the subsequent procedure being as above.
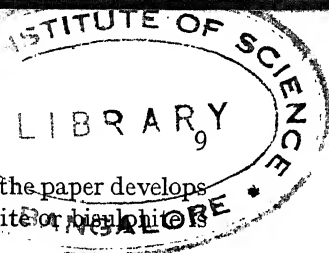
latter, and is then allowed to cool.   If a blue coloration of the paper develops after half an hour, the presence of sulphur dioxide, sulphite or bisulphite is assumed.

When the qualitative test gives positive results and a *quantitative determination* is required, the procedure is as follows :

50 grams of the meat are mixed to a paste with 100 c.c. of boiled water and 20 c.c. of 25% phosphoric acid added.   The flask is closed with a two-holed stopper through which pass (1) a tube dipping into the liquid and serving for the passage of a current of carbon dioxide, and (2) a tube connected with a condenser which dips, at the far end, below the surface of 100 c.c. of a solution of iodine in potassium iodide.[1]   About one-half of the liquid is distilled and the distillate acidified with hydrochloric acid and precipitated with barium chloride in the usual way : 1 gram of $BaSO_4$ = 0·2748 gram of SO_2.

(*f*) FLUORIDES. 25 grams of the sample, weighed in a platinum dish, are mixed with a certain amount of milk of lime, dried on a water-bath and incinerated ; the ash is introduced into a small platinum crucible and moistened with a few drops of water and then 1 c.c. of conc. sulphuric acid.   The crucible is covered with a watch-glass coated on the lower surface with wax, which is partially scraped away ; the crucible is then heated in an asbestos card and the glass examined to see if it is etched at the exposed places.

(*g*) SALICYLIC ACID.   10 grams of the meat are well shaken with 20 c.c. of alcohol and, after a few minutes, filtered, a few drops of dilute ferric chloride solution being added to the filtrate : a reddish-violet coloration indicates salicylic acid or one of its derivatives.

If a doubtful result is obtained, as may be the case when the salicylic acid is in very small quantity, the test is repeated as follows : [2] About 50 grams of the meat are weighed in a beaker and mixed with sufficient 2% sodium carbonate solution to give a homogeneous paste.   After standing for a time, the beaker, covered with a watch-glass, is left on a boiling water-bath for half an hour, during which time it is frequently stirred.   The hot mass is filtered through a piece of linen and the residue well pressed ; the filtrate is treated with 5 grams of sodium chloride, acidified with dilute sulphuric acid, and heated to incipient boiling.   When cold, the liquid is filtered and the filtrate shaken vigorously with an equal volume of a mixture of ether and petroleum ether (equal volumes) in a separating funnel.   The aqueous liquid is removed, and the ethereal solution washed two or three times with 5 c.c. of water and then filtered through a dry filter into a porcelain dish.   After addition of 1 c.c. of water, the ethereal solution is evaporated at a gentle heat.   To the residue are added a few drops of a freshly prepared 0·05% ferric chloride solution : in presence of salicylic acid, the characteristic violet coloration is formed.

(*h*) BENZOIC ACID.[3] 50 grams of the meat are vigorously shaken

[1] The solution is prepared by dissolving 5 grams of pure iodine and 7·5 grams of potassium iodide in a litre of water.

[2] Beythien : *Handbuch der Nahrungsmitteluntersuchungen*, Vol. I, p. 104.

[3] Fischer and Gruenert : *Zeitschr. Unt. Nahr- und Genuss-mittel*, 1909, XVII, p. 721.

in a beaker with 100 c.c. of 90% alcohol, then acidified with sulphuric acid, left for half an hour and filtered through linen, the residue being well pressed. The liquid is rendered alkaline with potash, heated on a water-bath to expel the alcohol, acidified with dilute sulphuric acid and heated to incipient boiling. After cooling the liquid is filtered, the filtrate shaken with ether, the ethereal solution washed with water, and the ether evaporated at a gentle heat. The residue is subjected to the following tests for benzoic acid :

1. Part of the residue is dissolved in a little water, the solution being treated with a drop of 2·5% ferric chloride solution and a drop of 3% hydrogen peroxide solution diluted with nine volumes of water and heated on the water-bath : a violet coloration indicates benzoic acid (oxidation to salicylic acid).

2. Another part of the residue is dissolved in a few drops of caustic soda solution, the liquid acidified and poured into a watch-glass, a granule of sodium amalgam added, and the glass covered with another. After a short time—as soon as reduction takes place—the odour of benzaldehyde is evident, even if only 1 milligram of benzoic acid is present.

8. Detection of Colouring Matters.—Colouring matters are added sometimes to mask defects due to changes in salted meats, sausages, etc. They are tested for as in meat (7, p. 2).

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It should be pointed out that the salt used in salting meat (in Italy) in some cases contains small quantities of boric acid ; experience shows that the amount of boric acid which can find its way into prepared meats from this source does not exceed 0·02%.

MEAT EXTRACTS

Meat extracts are more or less concentrated aqueous extracts of muscular flesh freed from coagulable albuminoid substances. They contain, therefore, in a more or less reduced volume, all the water-soluble principles of lean meat, and they have the appearance of a stiff, reddish-brown mass, with a rather bitter taste and a peculiar, not unpleasant odour (*Liebig's extract type*).

Besides genuine meat extracts, there are sold meat extracts mixed with vegetable extracts (*mixed extracts*) or extracts formed from various ferments and vegetable extracts, or vegetable extracts alone.

Analysis of meat extract has the same objects as that of fresh meat or sausages, namely, to determine the composition and nutrient value of the extracts and to detect adulterations and preservatives. With extracts of the Liebig type, determinations should always be made of the water, ash, potassium, fat and total nitrogen, while tests should be made for nitre and preservatives. Further, it is always useful to determine the various forms of combination of the nitrogen, especially the creatinine and the ammonia (*see* 7, 8 and 9, below). In mixed extracts, besides determinations of the

water, ash, potash, etc., tests for creatinine and yeast extract should also be made (*see* 9 and 10, below).

1. Determination of the Water.—The extract is removed from the containing vessel and thoroughly mixed, especially if liquid. From 2 to 3 grams of a solid or syrupy extract or 10 grams of a liquid one are weighed in a fairly wide, flat porcelain dish, which has been previously weighed together with 40 grams of well-washed sand and a glass rod. The mass is mixed with a rod—a little water being added if the extract is not already liquid—and heated on a boiling water-bath with occasional stirring of the mass until the latter assumes a homogeneous aspect. The dish is then dried in an air-oven at 100–105° to constant weight, the weighing being carried out as rapidly as possible.

2. Determination of the Ash.—About 10 grams (or more with a liquid) of the extract are weighed in a platinum dish and carefully incinerated in the manner indicated for meat.

3. Analysis of the Ash.—The usual determinations are those of the sulphuric acid, potassium (calculated as oxide), phosphoric acid and chlorine.

(*a*) DETERMINATION OF THE SULPHURIC ACID. A weighed quantity of about 0·3 gram of the ash is heated in a beaker with a little concentrated hydrochloric acid, then diluted with water and treated with barium chloride in slight excess. The precipitate is allowed to settle and is then filtered and washed, the filtrate and washings being used for the subsequent determination (*b*). The barium sulphate precipitate is weighed as usual and the percentage of sulphuric acid in the ash calculated.

(*b*) DETERMINATION OF THE POTASH. The filtrate and wash waters from (*a*) are evaporated to dryness in a porcelain basin on a water-bath. The residue is dissolved in water and the solution treated in a beaker with baryta water and boiled gently for some time. The solution is filtered and the filtrate treated with ammonia in slight excess, ammonium carbonate and a little ammonium oxalate ; the liquid is again filtered, the precipitate being washed with distilled water and the filtrate collected in a porcelain dish and evaporated to small volume. The liquid thus concentrated is filtered if necessary and poured into a platinum dish, into which also the porcelain dish is rinsed out with small quantities of water. The liquid is then evaporated to dryness and the residue carefully heated over a flame to expel the ammonium salts. At this point it is advisable to dissolve the residue in a very little dilute hydrochloric acid and to repeat the treatment with baryta and with ammonium salts, smaller quantities of the reagents being now used.

The residue free from ammonium salts may be weighed to obtain the total alkali chlorides. The residue is then evaporated almost to dryness with platinic chloride solution, 90–96% alcohol being then added ; the whole is well mixed with a glass rod and the potassium platinichloride collected on a tared filter (the filtrate should be deep yellow), washed well with 80–90% alcohol, dried at 130° and weighed. The weight found, multiplied by 0·194, represents potash (K_2O). The soda may be found from the weight of total alkali chlorides, by difference.

(*c*) PHOSPHORIC ACID. For determining phosphoric acid and chlorine

a new quantity of ash is prepared from 10 grams of the extract mixed with sodium carbonate. The ash is heated with a slight excess of nitric acid and then evaporated to dryness, the residue being taken up in dilute nitric acid and the volume made up with distilled water to a definite volume, say 500 c.c.

In an aliquot part of this solution (100 or 150 c.c.) the phosphoric acid is determined either by the ammonium molybdate method or as magnesium pyrophosphate (*see* Vol. I, p. 132).

(*d*) CHLORINE. In another aliquot part of the same solution, the chlorine is estimated gravimetrically.

4. Detection of Potassium Nitrate.—About 5 grams of the extract (15 grams if liquid) are diluted with 20 c.c. of distilled water and the liquid mixed with 10 c.c. of 20% sulphuric acid and distilled, the distillate being collected in 10–20 c.c. of a dilute sodium bicarbonate solution. The distillation is continued until the substance begins to bump, the distillate being then evaporated to small volume, acidified with dilute sulphuric acid and tested for nitric acid by means of ferrous sulphate or brucine in the usual way (*see also* p. 7).

For amounts of potassium nitrate higher than 0·1% the reaction is sharp and intense. A feeble coloration with brucine or a slightly coloured ring with ferrous sulphate should be neglected, since extracts may derive traces of nitric anhydride from the water used in their preparation ; such quantities, however, never amount to 0·1% of the extract.

5. Determination of the Fat.—This is carried out as for meat, the dry substance obtained as in I (above) being extracted with ether or petroleum ether (*see* p. 1).

This determination is superfluous with extracts which dissolve completely in water to a clear liquid.

6. Determination of the Total Nitrogen.—The method given for meat is followed (*see* p. 2), a quantity of extract corresponding with not more than 1 gram of dry substance being employed.

7. Determination of the Various Forms of Nitrogen.—In some cases it is useful to ascertain the percentages of certain nitrogenous compounds, the following methods being used :

(*a*) INSOLUBLE ALBUMINOIDS. From 10 to 20 grams of the sample, if solid or syrupy, or 25–50 grams if liquid, are dissolved in 100–200 c.c. of cold water. If solution is incomplete, the liquid is filtered through a tared filter and the residue washed on the filter with distilled water. The filtrate is used for determination (*b*), while the insoluble residue [1] is dried and weighed. Determination of the nitrogen in this residue by Kjeldahl's method and multiplication by 6·25 give the quantity of insoluble albuminoids.

(*b*) COAGULABLE ALBUMIN. The filtrate from the insoluble albuminoids or the aqueous solution of the extract, if the latter is entirely soluble, is acidified slightly with acetic acid and heated to boiling. The flocculent

[1] The residue may be examined microscopically for starch granules. If these are present, their amount may be determined by subtracting from the total weight of the residue that of the albuminoids determined as above.

albumin which separates is filtered off, washed with hot water and dried and the amount of nitrogen determined by Kjeldahl's method ; the quantity of nitrogen, multiplied by 6·25, gives the amount of coagulable albumin.

(c) ALBUMOSES. The liquid separated from the coagulable albumin, with the wash water, is made up, after cooling, to 500 c.c. with distilled water. In 50 c.c. the albumoses are determined as follows [1] :

The liquid is acidified with dilute sulphuric acid and saturated with finely powdered zinc sulphate, only a small portion of the salt being left undissolved. The albumoses, which separate at the surface of the liquid, are collected on a filter, washed with saturated zinc sulphate solution faintly acidified with sulphuric acid, and dried in an oven. The nitrogen in the dry substance is determined as usual : N × 6·25 = albumoses.

The amount of nitrogen thus found may contain that due to any gelatine added to the extract, this, like albumoses, being precipitated by zinc sulphate.

(d) NITROGEN OF MEAT BASES. To the liquid freed from the albumoses (see c), sodium phosphotungstate solution [2] strongly acidified with sulphuric acid is added until the precipitation is complete. After twelve hours the precipitate is filtered off and washed with dilute sulphuric acid, the wet filter-paper and precipitate being treated with sulphuric acid for the determination of the nitrogen by Kjeldahl's method. From the quantity of nitrogen found must be subtracted that in the form of ammonia (e).

This method precipitates, besides the bases, also any peptones present.

(e) AMMONIA. 200 c.c. of the solution prepared as in (c) for determining the albumoses are diluted with distilled water to about double the volume. Calcined magnesia is added and the liquid distilled, the ammonia in the distillate being determined with N/10-acid as usual.

8. Peptones.—From 4 to 5 grams of the extract are dissolved in a little water, the liquid being filtered if necessary and the albumoses separated with zinc sulphate as described above. The filtrate is precipitated with sodium carbonate to remove the zinc and the zinc-free liquid almost neutralised with sulphuric acid and evaporated on a water-bath until sodium sulphate crystallises. When cold, the deposited salt is removed from the liquid and the latter treated with excess of sodium hydroxide and a few drops of 1% copper sulphate solution : in presence of peptones the liquid becomes violet-red.

9. Detection and Determination of Creatinine.—This investigation is of particular importance in testing for meat extract in other preserves or in vegetable or yeast extracts.

A. QUALITATIVE TEST. About 10 grams of a solid extract or 20 grams of a liquid one are dissolved in 100 c.c. of water, the solution being heated to boiling to coagulate any albumin present and then cooled to the ordinary temperature. Lead acetate is now added little by little until no further precipitation occurs, the liquid being filtered, freed from lead by means of

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[1] Bömer : *Zeitschr. analyt. Chem.,* 1895, p. 568.

[2] 120 grams of sodium phosphate and 200 grams of sodium tungstate dissolved in water to a litre.

hydrogen sulphide, again filtered and concentrated to small volume. In this liquid creatinine is tested for as follows :

(*a*) To the moderately dilute solution are added a few drops of a recently prepared very dilute solution of sodium nitroprusside (D 1·003) and a few drops of caustic soda : in presence of creatinine the liquid turns ruby-red and shortly afterwards yellow. If the yellow liquid is heated with excess of acetic acid, it becomes green and then blue owing to the formation of Prussian blue.[1]

(*b*) A little aqueous picric acid and a few drops of dilute caustic soda are added to the liquid ; in presence of creatinine a red colour forms which persists for some hours and becomes yellow on acidification.[2]

The latter reaction is given also by acetone and if this is found to be present, the liquid should be boiled before testing.

B. QUANTITATIVE DETERMINATION. The following colorimetric method, based on the reaction with picric acid,[3] is used :

Reagents :

(*a*) 1·2 gram of picric acid is dissolved in 100 c.c. of water.

(*b*) 10% caustic soda solution.

(*c*) N/2-potassium dichromate solution.[4]

Procedure. 10 grams of the substance are dissolved in 100 c.c. of distilled water ; to 10 c.c. of this solution are added 15 c.c. of (*a*) and 5 c.c. of (*b*). After five minutes the volume is made up to 500 c.c.

The solution thus prepared is compared in the Duboscq colorimeter with the 8 mm. layer of the dichromate solution.

The colours are matched as usual and the scale read ; if the thickness of the layer is *a* mm., the amount of creatinine (*x*) in a gram of the extract will be

$$x = \frac{8·1 \times 10}{a}.$$

If more than 0·016 gram of creatinine is found, the test is carried out on a solution of double the dilution. The determination should be carried out as rapidly as possible—in less than half an hour.

10. Determination of the Creatine.—Besides the creatinine, the creatine also should be determined, the method being as follows :

10 grams of the extract are dissolved in 100 c.c. of very dilute hydrochloric acid (about N/3), the liquid being heated on the water-bath for four hours and then neutralised with caustic soda. After cooling, the liquid is made up to 100 c.c., the subsequent procedure being exactly that followed in determining the creatinine.

[1] Weyl: *Ber. deutsch. chem. Ges.*, 1878, XI, p. 2175.

[2] Jaffé: *Zeitschr. f. physiol. Chem.*, 1886, X, p. 399.

[3] Baur and Barshall: *Zeitschr. Unt. Nahr-Genuss-mittel*, 1907, XIII, p. 353.

[4] According to the experiments of various authors, this solution exhibits the same colour as a liquid with a creatinine basis prepared as follows : 0·010 gram of creatinine is dissolved in a little water and the liquid treated with 15 c.c. of picric acid solution (*a*) and 5 c.c. of caustic soda ; it is then left at rest for five minutes and made up to 500 c.c. As regards intensity of coloration, a layer 8·1 mm. thick of this solution corresponds with one 8 mm. thick of N/2-potassium dichromate. In the colorimetric determination of creatinine, the dichromate solution is sufficient.

This determination gives total creatinine (that pre-existing + that formed from the creatine by the action of hydrochloric acid), so that the creatinine from the creatine is obtained by difference ; creatinine × 1·16 = creatine.

11. Examination for Yeast Extract.—Yeast extracts contain principally marked quantities of xanthine bodies (xanthine, adenine, carnine, etc.), but, unlike meat extracts, they contain no creatine or creatinine. It is hence easy to detect meat extract in mixtures of this with yeast extract ; the inverse problem, which is the one usually presenting itself, is not so easy. Of the different methods proposed to meet this case, some of which are empirical, the only one capable of giving reliable results is that of Micko,[1] based on the detection of a special substance of the nature of gum, found only in yeast extracts. This method is as follows :

A portion of the extract is dissolved in three parts of hot water, ammonia in slight excess being then added. The precipitate formed is filtered off and the cold filtrate treated with excess of a freshly prepared ammoniacal copper solution (100 c.c. of 13% copper sulphate solution mixed with 150 c.c. of ammonia solution and 300 c.c. of 14% caustic soda solution).

In presence of yeast extract, a dense precipitate forms and collects into a compact mass. This precipitate is filtered through linen, thoroughly pressed, and then dissolved in water acidified with a little hydrochloric acid, three times its volume of alcohol being added to the solution thus formed. In this way a substance is obtained which, in the dry state, is a very fine powder ; the latter is soluble in water to a clear liquid, shows adhesive properties, has the specific rotation $[a]_D = 90·1°$, and is converted by the action of acid into a fermentable, feebly dextro-rotatory sugar able to reduce Fehling's solution.

With pure meat extracts, the procedure gives no turbidity or precipitate, whilst an extract containing only 10% of yeast extract gives an abundant precipitate.

12. Alcoholic Extract, according to Liebig.—Liebig's original method for determining the substances insoluble in 80% alcohol, which has been much discussed, is as follows :

2 grams of the extract are dissolved in a beaker with 90 c.c. of water, 50 c.c. of 93% alcohol then being added. The precipitate which forms adheres strongly to the glass, so that the alcoholic liquid may be readily poured into a tared dish. The precipitate is washed with 50 c.c. of 80% alcohol, which is also placed in the tared dish, the whole solution being then evaporated on a water-bath at about 70° and the residue dried for 6 hours in an oven at 100°.

According to modifications which have been suggested, the precipitate should be washed at least three times with 80% alcohol and the drying should be more thorough, a long time (often 35 hours or more) being required for the complete elimination of the water.

13. Tests for Sugar and Dextrins.—10 grams of the extract are

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[1] *Zeitschr. Unl. Nahr- und Genuss-mittel,* 1904, VIII, 230.

dissolved in water, boiled to eliminate the albumin, defecated with lead acetate, excess of the latter removed by means of sodium phosphate, the volume made up to 100 c.c. with water and an aliquot part inverted in the ordinary manner. From the polarimetric readings before and after inversion, the saccharose is calculated by Clerget's formula (*see* Chapter on Sugars).

The readings give an indication of the presence or absence of dextrins and confirmation is attained by evaporating the aqueous solution to a syrupy consistency, mixing it thoroughly with 95% alcohol, separating the precipitate and dissolving the latter in water and again treating the solution with water. The precipitate is then tested for dextrins (*see* Dextrin, Chapter III of this volume).

1 . Tests for Antiseptics.—These are carried out as for sausages (*see* p. 6). Particular attention is to be paid to the tests for boric acid, salicylic acid, formaldehyde and sulphur dioxide, which are more likely than other preservatives to be present in meat extracts.

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Meat extracts should dissolve readily in water giving a clear or only slightly turbid liquid (pronounced turbidity is an indication that change has occurred); they should contain not more than traces of insoluble or coagulable albuminoids and should be free from fat, while the ethereal extract should not exceed 1·5%.

The *water*-content of the solid extracts sold rarely exceeds 21% (mostly 17–20%), whilst liquid extracts contain about 65% of water.

The *ash* of solid extracts amounts normally to about 20%, the limits being 17–25%. It is composed mainly of potassium phosphate with small proportions of sodium and potassium chlorides and calcium phosphate. The phosphoric acid is partly of organic origin and amounts to 23–38% of the ash. The chlorine, calculated as sodium chloride, should not exceed 15% of the ash. The potassium salts, calculated as oxide, vary between 32 and 46% of the ash, or 6–12% of an extract with the normal content of water (17–21%).

The *organic matter* of the extract, found by deducting from 100 the percentages of water, ash and fat, amounts to 58–62% and is composed mostly of albuminoids, of which a considerable part (corresponding with about one-half of the total nitrogen) has not yet been identified.

Non-nitrogenous organic substances are present in small quantity, the principal ones being glycogen (up to 1·5%), inositol, sarcolactic acid, butyric acid, etc.

The *total nitrogen* of extracts varies from 8·5 to 9·5%; at least 10% of the total nitrogen should be in the form of creatine and creatinine, which are the most characteristic chemical constituents of meat extracts. Albumoses also are normal components and vary between 5 and 10%, while the proportion of the total nitrogen in the form of xanthine bases should be 6–9%. The ammonia should not exceed 0·6% (mean of numerous analyses).

Alcohol of 80% strength (*Liebig's test*) should dissolve not less than 56% of the substance, and usually dissolves 61–64%.

Sugar and *dextrins* are not present in normal extracts, and the ordinary preservatives should not be found.

TINNED MEATS

With these the analysis has the same object as with sausages and meat extracts, namely, the determination of the nutritive value and the detection of any adulteration or change. The determinations made, either separately on the liquid and meat or on the product as it stands, are those of the water, ash, fat, nitrogen, acidity of the fat, horseflesh, starch, colouring matters and antiseptics, the methods given under sausages being followed. In this case special importance attaches also to the examination of the external characters of the tin and to the test for metals.

1. External or Objective Characters.—The tin should have more or less concave ends, indicating that the vacuum has been maintained ; if the ends are convex and swollen, it may be assumed that the interior has undergone change.

When the tin is opened, the reaction is tested in different parts of the product with litmus paper ; the reaction should be faintly acid, any marked alkalinity rendering the product suspicious. The liquid should be gelatinous and transparent and its odour and taste and also those of the meat should be normal and pleasant. The internal condition of the meat is examined, the colour and consistency of a fresh cut and any formation of gas-bubbles being noted.

Advanced decomposition is indicated immediately by the smell of ammonia and sometimes of hydrogen sulphide, and more often by the unpleasant odour of indole and scatole. Incipient decomposition is detected by bacteriological examination, which is useful in all cases.

2. Detection of Heavy Metals.—The interior of the mass is examined with a lens for metallic globules (sometimes entering during soldering), which should be collected and analysed in the usual way. Qualitative examination of the interior of the mass for heavy metals is carried out as follows :

About 50 or 60 grams of the sample, obtained by mixing the contents of one or more tins intimately with a mincer, are weighed in a porcelain dish, dried on a water-bath and carefully incinerated. The ash is evaporated to dryness with concentrated nitric acid and the residue taken up in very dilute nitric acid and filtered. The residue on the filter is tested for tin and antimony by the ordinary methods. The filtrate is evaporated to dryness with conc. hydrochloric acid, the residue being then taken up again in water acidified with hydrochloric acid and the solution tested for lead, copper, zinc, etc.

3. Determination of the Copper and Zinc.—One or more tins are emptied into the feeder of a mincing machine and the whole thoroughly triturated, 100 grams being then dried in an oven and carefully incinerated and the ash heated with excess of conc. nitric acid and evaporated on a water-bath until the acid is completely expelled. The residue is heated with distilled water and a drop of dilute nitric acid, the liquid being filtered and any carbonaceous residue on the filter well washed with water.

The filtrate is evaporated on a water-bath to about 50 c.c. and then

diluted with its own volume of absolute alcohol and acidified with excess of dilute sulphuric acid, which precipitates the lead as sulphate. After 1–2 hours, the precipitate is collected in a Gooch crucible, washed with alcohol until the filtrate is neutral, dried, heated in a roomy porcelain crucible in an air-oven and weighed : $PbSO_4 \times 0.683 = Pb$.

The filtrate from the lead sulphate is evaporated on a water-bath until the alcohol is eliminated and the copper then determined either electrolytically (see Vol. I, p. 230) or as sulphide by Rose's method.

4. Arsenic.—50 grams of the minced sample are weighed into a round-bottomed flask and heated over a naked flame with 10 c.c. of concentrated sulphuric acid ; when the mass becomes dense, 30 c.c. of the same acid are added, the heating being continued and further small quantities of acid added until the liquid is completely decolorised. When cold, the solution is poured carefully into 150 c.c. of cold water, the resulting liquid being filtered and the filtrate tested for arsenic in the Marsh apparatus (see later, 5, b) and also for any other metals (zinc, nickel, etc.).

To destroy the organic matter and to test subsequently for arsenic zinc, etc., Gasparini's method [1] may be followed with advantage :

50 grams of the substance are completely covered with pure concentrated nitric acid in a tall, wide beaker, which is covered with a large clock-glass perforated by two holes arranged symmetrically and 6–7 cm. apart. Through the holes pass two glass rods with sheet platinum electrodes at the ends, these being connected with the outside by platinum wires passing along the glass rods. The electrodes are bent at right angles to the rods and one lies at the bottom of the beaker and the other just below the surface of the nitric acid. The substance is left in contact with the acid for some hours, the current being then applied : 4–6 amps. at 8 volts. The passage of the current is continued until the liquid becomes clear and bluish and the layer of fat, which soon rises to the surface, is considerably reduced in volume. After cooling, the layer of fat is separated by filtration and washed by heating repeatedly with water acidified with nitric acid, shaking, allowing to cool and filtering by decantation. The wash waters are added to the filtrate and the whole evaporated to dryness in a porcelain dish. The residue is taken up in water and the clear, yellowish liquid thus obtained tested for arsenic in the Marsh apparatus.

5. Test of the Tinning of the Metal.—Tests are made especially for lead and arsenic in the internal tinning.

(a) LEAD. Part of the tin free from solder is cut with shears, and the tinned part washed with alcohol and ether and dried. Two or three drops of concentrated nitric acid are dropped upon it, the part treated being gently heated after a minute or two until all the acid is driven off. When cold, the white spot is moistened with 5% potassium iodide solution ; in presence of lead, a yellow coloration, due to lead iodide, is formed. With this procedure, if the tinning is very slight, the nitric acid may attack the iron beneath the layer of tin, so that a coloration may then be given owing to the formation of ferric iodide ; in such case the presence of lead should be confirmed, thus :

[1] *Gazzetta chimica italiana*, 1905, i, p. 501.

Another portion of the tin, prepared and washed as above, is treated with nitric acid diluted with an equal volume of water and heated almost to boiling. This treatment is carried out in a porcelain dish by pouring the hot acid on to the tinned part of the metal, which is rubbed with a glass rod fitted with a band of rubber ; after mixing, the metal is removed and washed with a little water, the acid liquid being evaporated to dryness. The residue is taken up in water rendered very faintly acid with nitric acid, the stannic acid being removed by filtration and the filtrate treated with slight excess of ammonium sulphide and heated almost to boiling. Any precipitate formed is collected on a small filter, washed, and dissolved in a little dilute nitric acid, the solution being evaporated to dryness, the residue dissolved in hot water, and a few drops of potassium chromate solution added : in presence of lead, a yellow precipitate (lead chromate) is obtained.

For the *quantitative* determination of the lead, the method given for tin-plate (*see* Vol. I, p. 256) is followed.

(b) ARSENIC. A certain quantity of the tin, as free as possible from the metal beneath, is scraped off and evaporated to dryness with pure nitric acid free from arsenic, the residue being taken up in a little pure sulphuric acid and heated until white fumes disappear. When cold, the liquid is diluted with 2–3 volumes of distilled water and tested for arsenic in the Marsh apparatus.

Marsh's method for testing for arsenic is based on the fact that, under the action of nascent hydrogen, all arsenical compounds are transformed into hydrogen arsenide, which is decomposed with deposition of arsenic when heated.

The apparatus used takes several different forms, one of the simplest consisting of a two-necked Wolff's bottle, a thistle funnel being fitted into one neck and a gas delivery tube, connected with a calcium chloride tube, into the other. Beyond the calcium chloride tube is a hard *glass tube*, 40–45 cm. long and 5–6 mm. in diameter, drawn out at a certain position to a narrow, pointed tube.

When the apparatus is assembled, the Wolff's bottle is placed half in cold water and is charged with pure zinc and dilute sulphuric acid (1 part of conc. acid + 4–5 parts of water), the evolution of hydrogen being allowed to proceed until all the air is expelled from the apparatus. The hard glass tube is then heated to redness with a bunsen flame about 10 cm. wide to ascertain if any shining grey or black ring forms at the constricted part ; if not, the freedom of the zinc and acid from arsenic is presumed and the actual test made.

To this end, the action of the zinc on the acid is not interrupted, but the solution to be examined is introduced into the apparatus by way of the funnel in small portions at intervals of about 10 minutes. If arsenic is present, a brownish and then shining black ring soon develops in the narrow tube at a short distance from the heated point, the intensity of the deposit increasing with the amount of arsenic present.

Under proper conditions—the tube being heated to redness, the evolution of gas slow and regular, and the addition of the liquid gradual—the

decomposition of the hydrogen arsenide will be complete and the whole of the arsenic will be found deposited in the tube. The weight of the arsenic may be determined by cutting off and weighing the portion of the tube containing the ring and then dissolving the latter in nitric acid and again weighing the dried tube.

In most cases the amount of the arsenic is not required ; after the ring has been obtained, the heating may then be discontinued and the issuing gas ignited at the end of the tube. If the quantity of arsenic is not very small, the flame assumes a livid, violet colour and an alliaceous odour is emitted, while a shining brownish-grey or black spot forms on a piece of porcelain held in the flame. The porcelain should be moved from time to time to avoid excessive heating and consequent volatilisation of the arsenic, several spots being obtainable in this way.

It is advisable to make sure that the rings and spots consist of arsenic and not of antimony : this may be done :

(1) By treatment with calcium or sodium hypochlorite solution, which dissolves arsenic stains readily, whereas antimony is dissolved only after a long time.

(2) By treatment with concentrated sodium nitroprusside solution, in which arsenic is insoluble, while antimony is soluble.

(3) By treating the spot with hot nitric acid, evaporating to dryness on a water-bath, dissolving the residue in two drops of water and adding ammoniacal silver nitrate solution (2 or 3 drops) : in presence of arsenic a brick-red precipitate of silver arsenate is formed.

Marsh's method is extremely sensitive, being capable of detecting 0·001 milligram of arsenic.

6. Examination of the Solder from the Tin.—The solder to be examined is that found in the inner part of the tin. It is either cut from the tin and then melted or heated by means of a bunsen flame until it drops into an unglazed porcelain crucible, in which it is fused to a homogeneous button. In this the lead is determined by one of the following methods :

(a) DETERMINATION BY THE SPECIFIC GRAVITY. If there is sufficient of the alloy (about a gram), the latter is hammered to remove any internal irregularities or spaces, and its specific gravity then measured by the usual methods. If the value found equals or exceeds 7·70, the alloy contains more than 10% of lead ; if it is between 7·60 and 7·70 (which indicates 10–15% Pb) it is advisable to determine the lead quantitatively ; if it is less than 7·60, the alloy certainly contains below 10% of lead.[1]

This method, based on the variability of the specific gravity of tin-lead alloys according to their composition, is rapid and gives approximately the proportion of the lead.

(b) QUANTITATIVE DETERMINATION OF THE LEAD. The procedure is as given for lead-tin alloys (see Vol. I, p. 258).

7. Examination of the Rubber.—If rubber rings are used for closing the tins, they should be examined for lead, zinc, and other metals.

[1] S. Grimaldi : *Staz. sper. agrar. italiane*, 1904, p. 1026 ; G. Giusti : *idem*, 1905, p. 820.

The rubber is incinerated, the ash treated with a small quantity of nitric acid and boiling water, the liquid filtered and the filtrate analysed by the usual methods.

For a more exact examination the procedure is as follows :

About 2 grams of a mixture of sodium carbonate and potassium nitrate are melted in a porcelain crucible and about 1 gram of the substance, finely cut, gradually added to the fused mass. When cold, the mass is heated with water and the clear liquid decanted off, the residue being subsequently boiled with two separate quantities of 50 c.c. of water and filtered. The lead and zinc are left as carbonates and, after solution in acetic acid, may be identified in the usual way. The presence of zinc is also shown by the yellow colour of the hot, fused mass.

For the detection of antimony and mercury, *see* Vulcanised Rubber, 5 (Chapter XI, this volume).

CHAPTER II

MILK AND ITS PRODUCTS

Milk yields principally the two highly important products, butter and cheese ; both of these and also milk itself, including preserved and condensed milks, are dealt with in the present chapter.

MILK

Milk is an aqueous and partly colloidal solution of casein, albumin, lactose and mineral salts, intimately emulsified with fatty substances.[1]

The milk which forms such an important article of diet and for which analysis is most frequently required is that of the cow.

Its most common adulterations consist of *dilution* and *removal of cream*. It may also be mixed with various extraneous substances (occasionally flour, starch, dextrin, albumin, etc.) or treated with antiseptics (boric acid, borax, salicylic acid, formaldehyde, benzoic acid, fluorides, hydrogen peroxide, etc.) to make it keep, or with alkaline salts (sodium carbonate or bicarbonate) to hinder or correct for fermentation. Analysis of milk includes, therefore, the following determinations :

Sampling and Storage of the Sample.—Before analysis, the sample should be well mixed, either by pouring it repeatedly from one vessel to another, but avoiding the formation of froth, or by stirring it vertically, slowly and without beating it, with a rod fitted at the end with either a perforated disc or a metal bucket.

If sampling is not followed immediately by analysis, the sample must be treated with a preservative, but not such as to falsify the analytical results : use is made of 10% potassium dichromate solution, formaldehyde, hydrogen peroxide, alcoholic solution of phenol, mercuric chloride (about 5% solution), etc., a few drops being added. The last of these preserves milk very well for several days without altering its composition or disturbing the determinations, but its poisonous character necessitates precautions.

1. Objective Characters.—Note is made if the milk has the normal pleasant taste and smell : if it is bitter, acid, soapy, salty (altered) ; if it has the normal opaque white colour and is not yellowish, reddish or bluish (altered). Its reaction to litmus paper should be amphoteric.

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[1] Another definition of milk, based on its origin, is as follows : Milk is a liquid secreted by the mammary gland, as a result of uninterrupted and complete milking ealthy animals, at least eight days after parturition (Fascetti : *Caseificio*, p. 36).

2. Specific Gravity.—This can be determined in the usual way, with the Westphal balance, the picnometer, or the densimeter, at 15°. The following procedure is the most common and is carried out on the milk as it stands or on the whey.

(a) ON THE MILK: Use may be made of *Quevenne's lacto-densimeter*, which is a hydrometer (Fig. 1) with the stem divided into 29 parts between 14 and 42, each division corresponding with 0·001 above unity; thus the division 32 indicates the density 1·032. It is furnished also with a thermometer, the scale of which is usually prolonged above the graduated stem. The latter carries two conventional graduations showing approximately the quantity of water added to the milk in correspondence with the density indicated; the yellow scale is used for the whole milk, and the blue one for milk free from cream. At a temperature of exactly 15°, the densimeter gives the true density of the milk, but for other temperatures use is made of tables of corrections, one for the whole milk and another for skim milk; if the temperature is not very far from 15° (not more than about $\pm$ 5°), 0·0002 (or 0·2° on the lacto-densimeter) may be added to or subtracted from the density found for each degree of temperature above or below 15°.

The well-mixed milk is poured into a glass cylinder standing on a flat surface so that no froth is formed and the lacto-densimeter introduced into the middle of the liquid. After two minutes the specific gravity is read off, the observer looking along the free surface of the milk and at right angles to the graduated stem.

FIG. 1

This method is easy and rapid and very useful as a preliminary; it also serves as a good guide for inspectors charged with taking samples of milk. It may, however, lead to erroneous conclusions when it is not known if whole or skim milk is being dealt with.

(b) IN THE WHEY: 150 c.c. of the milk are heated to 40–50°, 2 c.c. of a very concentrated solution (D 1·030–1·032) of tartaric acid in 85% alcohol being added; the heating is then stopped, the liquid stirred with a glass rod to collect the coagulum and filtered through a fine linen or woollen cloth. The filtered whey is poured into a cylinder, left to cool in the air or immersed in cold water, and the density determined at 15°.

3. Dry Solids.—These are estimated as follows:

(a) DIRECTLY. 10 grams of the milk are weighed in a flat porcelain, nickel or platinum dish about 70 mm. in diameter, evaporated to dryness on a water-bath, and the drying finished in an air-oven at 100–105° for 2½ hours: (weight obtained) × 10 = percentage of total solids.

In the Italian Official Method (1905), the milk is mixed, before evaporating, with about an equal weight of paper, previously dried and extracted with petroleum ether, or a somewhat greater weight of powdered pumice.

(b) INDIRECTLY. The percentage of total solids (x) is given by Fleischmann's formula:

$$x = 1\cdot2g + 2\cdot665\frac{100p - 100}{p},$$

where g = percentage of fat and p = specific gravity of the milk.

The trouble of calculation may be avoided by the use of suitable tables such as that of Siats or by Ackermann's metal disc calculator.

4. Solids not Fat.—This is the difference between the percentages of dry solids (x) and fat (f).

5. Fat.—This may be determined either volumetrically or gravimetrically.

(a) VOLUMETRIC METHODS. These are based on the mechanical separation of the fat by suitable means, of which that most commonly used is Gerber's acido-butyrometer; the procedure is as follows:

Reagents: (1) Pure sulphuric acid (D 1·820–1·825 at 15°).

2. Pure amyl alcohol (D 0·815–0·818), b.pt. 124–130°, which is tested by a blank experiment.

Apparatus: (a) Butyrometer with a single aperture (see Fig. 2), graduated so that each division corresponds with 1% of fat in the milk.

(b) Pipettes: 1 c.c. for the amyl alcohol, 11 c.c. for the milk, and 10 c.c. for the sulphuric acid.

(c) Centrifuge, consisting of a circular disc (see Fig. 3), fitted with a
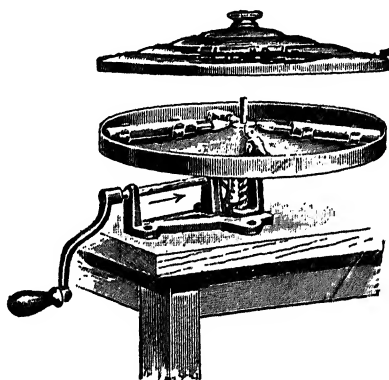

FIG. 2

FIG. 3

FIG. 4

cover and with metal clips for the butyrometer tubes and rotatable by hand or mechanically.

Procedure. Into the butyrometer tube 10 c.c. of the sulphuric acid and then 1 c.c. of the amyl alcohol are pipetted [1] without mixing; as quickly

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[1] The glass apparatus used should always be well cleaned with 10% caustic soda ⁖ion.

as possible 11 c.c. of the milk are next introduced, the tube being closed with a rubber stopper and well shaken. This causes marked heating and dissolution of the albuminoids of the milk in the acid. The tube is then left in a water-bath at 65–70° for about ten minutes, after which it is dried and fitted in the centrifuge and rotated for 2 minutes and left in the water-bath again for 4–5 minutes. The volume of the fat collecting at the top of the liquid, as shown on the stem of the tube, gives the percentage of fat in the milk.

With skim milk the centrifugation and preceding heating should be repeated several times and specially exact butyrometers (*see* Fig. 4) should be used, with the upper part of the tube only $\frac{1}{10}$ or $\frac{1}{100}$ as large as usual.

(*b*) GRAVIMETRIC METHODS. In these the fat extracted from the milk by a solvent is weighed.

According to Rose and Gottlieb, 10 c.c. of the milk and 2 c.c. of ammonia (sp. gr. 0·960 : about 95 NH_3 per 1,000) are treated in a 100 c.c. cylinder, graduated to 0·5 c.c., with 10 c.c. of 95% alcohol. The cylinder is closed and its contents thoroughly mixed by repeated inversion and shaken after addition of 25 c.c. of anhydrous ether and again after addition of 25 c.c. of pure petroleum ether (b.pt. 60°). After an hour's rest, as large an aliquot part as possible of the ethereal fat solution—which must be quite clear—is extracted by means of a pipette or small syphon or otherwise, the volume before and afterwards being read off. The solution removed is carefully evaporated in a tared vessel on a water-bath and the residue dried at 100° and weighed : the weight gives the amount of fat in the aliquot part of the solution removed.

According to the Official Italian Methods (1905), the fat is estimated, besides by the above acido-butyrometer, also by weighing, 10 grams of the milk being mixed with 5 grams of paper pulp, dried (*see* 3, above), extracted in an extraction apparatus with ether and the residue from the ethereal solution dried for 4–5 hours at 100°.

6. Nitrogenous Substances.—These consist mainly of proteins (casein, albumin) and to a small extent of other substances (lecithin, etc.). They may be determined together or separately from the nitrogen estimated by the Kjeldahl-Ulsch method (Vol. I, p. 122) :

(*a*) TOTAL NITROGENOUS SUBSTANCES. 20 grams of the milk are evaporated to dryness in a Kjeldahl flask by immersing the latter in a water-bath, the residue being then heated with 20 c.c. of the phosphoric-sulphuric acid mixture and a drop of mercury : nitrogen × 6·37 = total nitrogenous compounds.

(*b*) CASEIN. 20 grams of the milk are diluted with 80 c.c. of saturated magnesium sulphate solution and the mixture thus obtained completely saturated with solid magnesium sulphate ; the precipitate formed is filtered off and washed 7 or 8 times with saturated magnesium sulphate solution, the nitrogen contained in it being then estimated by the Kjeldahl method : nitrogen × 6·37 = casein.

(*c*) ALBUMIN. Determined indirectly by deducting the casein from the total nitrogenous substances.

According to the Official Italian Methods (1905), the total proteins of the milk are determined by evaporating 5–10 grams of the milk to dryness in a

flask, treating the residue with 20 c.c. of phosphoric-sulphuric acid mixture and 1 gram of copper oxide, determining the nitrogen in the usual way and multiplying by 6·37.

7. Lactose.—20 grams of the milk, in a 100 c.c. measuring flask, are diluted with about 60 c.c. of water, heated on a water-bath, treated with 3–4 drops of concentrated acetic acid, shaken and heated until the albuminoid matters are separated, these carrying down also the fat ; after cooling to 15° the liquid is made up to the mark with water, shaken and filtered. In the filtrate the lactose is determined by means of Fehling's solution (5 c.c. of copper solution, 5 c.c. of alkaline tartrate, 40 c.c. of water) as described in the chapter on sugars, the liquid being boiled for 6 minutes.

The percentage of hydrated lactose (l) is given by :

$$l = \frac{6·76 \times 5}{n} = \frac{33·8}{n},$$

where n is the number of c.c. of sugar solution used.

8. Ash.—In a platinum dish on a water-bath 25 grams of the milk are evaporated to dryness and the residue carefully charred over a naked flame, the carbon being extracted with hot water and then completely burnt in the same dish. The liquid from the lixiviation is added and the whole evaporated on a water-bath, dried and calcined until quite white, the percentage of ash then being calculated.

A more rapid method is as follows : 10 grams of the milk plus a few drops of acetic acid are evaporated to dryness in a platinum dish and the residue incinerated and calcined at a dull red heat.

9. Acidity.—50 c.c. of the milk are titrated with N/4-sodium hydroxide solution in presence of 2 c.c. of 2% alcoholic phenolphthalein solution : the number of c.c. of N/4-soda necessary to neutralise 100 c.c. of the milk represents the degree of acidity of the milk.

Coagulated milk should be filtered, the coagulum washed with water and the filtrate titrated.

If it is desired to express the acidity of milk as lactic acid, the degree of acidity is multiplied by 0·0225.

10. Special Investigations.

(a) TEST FOR REDUCTASES. This serves, within certain limits, to indicate the purity and the extent to which the milk has kept good, the reducing power of milk being proportional to the number of micro-organisms present.

Into a test-tube are poured 40 c.c. of the milk and 1 c.c. of methylene blue solution (hydrochloride of the leuco-base of methylene blue) obtained by diluting 5 c.c. of concentrated, alcoholic, methylene blue solution with water to 200 c.c. The test-tube is kept in a water-bath at 38–40° and note taken of the time necessary to produce decoloration, the upper part of the milk in the tube being neglected. The conclusions to be drawn are :

1. *Very bad milk* : colour not maintained for more than 20 minutes.
2. *Bad milk* : colour maintained from 20 minutes to 2 hours.
3. *Medium quality milk* : colour maintained 2–5½ hours.
4. *Good milk* : colour maintained more than 5½ hours.

(b) CRYOSCOPIC INDEX. Use is made of Beckmann's apparatus (*see*

Fig. 5), which is generally employed for determining the freezing points of solutions. It consists of a tube furnished with a stirrer and with a very exact thermometer, divided into hundredths of a degree. This tube, containing the milk, is placed in an air-jacket and this in a vessel furnished with a stirrer and a thermometer and charged with a freezing mixture (3–4 parts of ice and 1 part of salt).

Sufficient of the milk, cooled to 0°, is placed in the tube to cover the thermometer bulb to a depth of about 1 cm. and stirred until the mercury ceases to fall, note being then made of the temperature, which is somewhat below the freezing point. After the tube has been withdrawn from the freezing mixture and warmed with the hand until the bulk of the ice formed has melted and the temperature has risen 0·5—0·6°, the experiment is repeated with constant stirring, the freezing point being taken as the lowest temperature then reached by the thermometer. It is, however, more usual to regard as the freezing point, not the lowest temperature shown by the thermometer, but that at which the thermometer remains constant for some time, this being rather higher than the point of greatest cooling.

The cryoscopic index is always determined on fresh milk, as it is influenced by the acidity of the milk, by heating it and by the addition of preservative or saccharine substances.

FIG. 5

(c) CORNALBA CONSTANT (*total soluble matter*). The dry residue of the milk is determined by evaporating 3–4 grams on a water-bath and then in a steam-oven to constant weight (about 4 hours), the result being referred to 100 grams of the milk. Next, 20 c.c. of the milk, diluted with 80 c.c. of water, are precipitated in the cold with 1 c.c. of 10% acetic acid, the liquid being filtered after some hours through a tared filter and the precipitate washed with 100–150 c.c. of water and dried in an oven to constant weight. The net weight of the precipitate is multiplied by 5 and the result, which represents the total undissolved constituents of the milk, subtracted from the dry residue to obtain the total soluble matter.

(d) REFRACTOMETRIC DEGREE OF THE WHEY. This is determined as follows [1]: A solution of calcium chloride is prepared which has exactly the specific gravity 1·1375 (corresponding with about 16% $CaCl_2$) and which, diluted 1 : 10, gives a refraction of 26° at the temperature 17·5°. In a special thin glass tube 30 c.c. of the milk and 0·25 c.c. of the calcium chloride solution are shaken vigorously, the tube being then closed with a suitable condenser and immersed in a boiling water-bath for 15 minutes. The tube is then left in water at about 17·5° until it assumes that temperature, the small quantity of water condensed in the upper part of the tube or in the condenser being united to the rest by carefully shaking, turning and slanting the tube. The whole is then poured into a small beaker and,
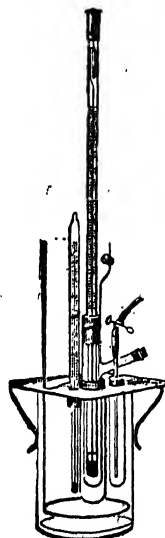
[1] Ackermann : *Zeitschr. Unt. Nahr- und Genuss-mittel*, 1907, I, p. 186.

without filtering, the whey examined in an immersion refractometer (e.g. Zeiss's) to determine its refractive index.

11. Preservatives and Antiseptics.—The most common preservatives are tested for as follows :

(*a*) SALICYLIC ACID. 100 c.c. of the milk are shaken with 100 c.c. of hot water (60°), 8 drops of acetic acid and 8 drops of mercurous nitrate solution and filtered, the filtrate being shaken with 50 c.c. of a mixture of ether and petroleum ether in equal volumes. The ethereal layer is then separated and the solvent evaporated, the residue being dissolved in a little water and treated with a few drops of a recently prepared 0·05% ferric chloride solution : a violet coloration indicates salicylic acid.

(*b*) BORIC ACID AND BORAX. 100 c.c. of the milk, rendered alkaline with sodium carbonate solution, are evaporated to dryness and the residue incinerated, the ash being moistened with hydrochloric acid and tested with turmeric paper : a red coloration indicates boric compounds.

(*c*) SODIUM BICARBONATE. This is detected by the distinct alkalinity of the milk, by the marked presence of sodium phosphate in, and the pronounced alkalinity of, the soluble part of the ash. If 5–10 c.c. of alizarin solution (0·2 gram per 100 c.c. of 90% alcohol) are added to 100 c.c. of the milk, a distinct red coloration is obtained in presence of sodium carbonate or bicarbonate, whereas pure milk gives a yellowish colour.

(*d*) FORMALDEHYDE. 100 c.c. of the milk are distilled with 1 c.c. of dilute (1 : 3) sulphuric acid, the first 20–25 c.c. of distillate being tested for formaldehyde as follows :

1. About 15 c.c. of the distillate are treated with 1 c.c. of aqueous 4% phenylhydrazine hydrochloride solution, 3–4 drops of freshly prepared 0·5% sodium nitroprusside solution and sufficient concentrated caustic soda solution to render the liquid alkaline : an intense blue coloration gradually, and especially on heating, changing to red, indicates formaldehyde.

2. To 10 c.c. of the distillate are added a small quantity (about 0·1 gram) of peptone and then a drop of 5% ferric chloride solution and 10 c.c. of conc. sulphuric acid, which is allowed to flow gently down the side of the tube so as to form two layers : a violet-blue ring forms between the two layers in presence of formaldehyde.

(*e*) FLUORIDES AND FLUOBORATES. About 200 c.c. of the milk are evaporated to dryness with lime and the residue incinerated, the ash being treated with water containing about 5% of acetic acid, which will dissolve any calcium borate present owing to addition of fluoborates to the milk. In the acetic acid solution, boric acid is tested for as previously described.

The residue from the treatment with acetic acid is again incinerated together with the filter, the ash being mixed with precipitated silica or calcium silicate or even finely powdered sand and introduced into a platinum crucible ; the mass is then moistened with a little concentrated sulphuric acid and the crucible immediately covered with a glass plate having a drop of water on its lower side. In case the ash contained fluorine compounds, there will appear, after a few moments and without heating, a deposit of silica on the edges of the water-drop.

The residue from the treatment with dilute acid may also be tested for hydrofluoric acid by the ordinary glass-etching method.

(*f*) BENZOIC ACID. From 250–500 c.c. of the milk are evaporated with a few drops of barium or calcium hydroxide to about one-fourth of its volume, powdered calcium sulphate being then added and the evaporation continued to dryness. The residue is finely powdered, moistened with a little dilute sulphuric acid and extracted three or four times with 50% alcohol. The combined alcoholic extracts are neutralised with barium hydroxide, evaporated to small volume, acidified with dilute sulphuric acid and extracted with ether; evaporation of the latter leaves almost pure benzoic acid, which may be identified by converting it into benzaldehyde or salicylic acid and testing for these by their specific reactions (*see* Meat, pp. 9 and 10).

(*g*) HYDROGEN PEROXIDE. This preservative disappears after a few hours, being decomposed by the milk, so that the reactions will not give positive results if a long time has elapsed since the addition.

1. To 10 c.c. of the milk are added three drops of a solution of 1 gram of recently precipitated vanadic acid in 100 c.c. of dilute sulphuric acid: a red coloration forms in presence of hydrogen peroxide.

2. To 10 c.c. of the milk are added 15 c.c. of raw milk known to be genuine and 3 drops of aqueous 2% paraphenylenediamine solution (freshly prepared): a blue colour appears in presence of hydrogen peroxide. This reaction is highly sensitive.

12. Detection of Boiled (Sterilised) Milk.

1. The milk is allowed to coagulate spontaneously or is treated with acetic acid, and then filtered, the clear filtrate being heated: if the liquid is rendered turbid in this way (by coagulation of albumin), the milk has not been boiled or indeed heated above 85°.

2. Solutions are prepared of (*a*) 1 gram of paraphenylenediamine in 50 c.c. of water and (*b*) 1% hydrogen peroxide solution, diluted with five times its volume of water and acidified with a few drops of very dilute sulphuric acid (1 c.c. of the conc. acid per litre). From 5 to 10 c.c. of the milk are treated with a drop of (*b*) and 2 drops of (*a*). With raw milk or milk which has not been heated above 78°, an intense blue coloration is formed immediately. With milk previously heated to 78–80°, a bluish-green coloration forms after a few moments. Milk heated above 80° gives no coloration, or at most a scarcely perceptible violet.

3. To 1 volume of the milk are added 1 volume of aqueous 1% guaiacol solution and a drop of hydrogen peroxide: raw milk gives a garnet-red coloration, which is not obtained with boiled milk.

* *
*

Pure, sound milk should have the normal colour, taste and smell; it should contain no extraneous substances, antiseptics or other preservative agents and should contain no pathogenic micro-organisms, which are detectable by bacteriological examination and by the behaviour towards the reductase test (*see* 10. *a*).

As regards the more common forms of adulteration, which consist in:

1. Addition of water,
2. Removal of cream,
3. Addition of skim milk,
4. 1 and 2 together,

use is made principally of the determinations of the specific gravity of the milk and of the whey, the fat and the solids not fat ; in case doubt still remains as to the genuineness of the milk, especially as to the presence of added water, the cryoscopic index, refractometric degree of the whey and the total solids may be determined.

In order to decide if a milk has been watered, the health authorities of Italian municipalities usually rely on the specific gravity, the fat and the solids not fat ; some use also the specific gravity of the whey, and very few the cryoscopic index.   The standards adopted by certain of these authorities are given in Table I :

<div align="center">TABLE I</div>

Municipality.	Specific Gravity of the Milk.	Specific Gravity of the Whey.	Total Dry Residue, %.	Fat, %.	Solids not Fat, %.
Ancona . . .	1·029–1·034	1·027	12	3	—
Bologna . . .	1·0275	—	11·75	3	8·75
Brescia . . .	—	—	12·50	3·50	9
Cagliari . . .	1·029–1·033	—	12–12·5	2·50	—
Florence . . .	1·029–1·034	1·027	—	3	—
Genoa	—	—	12	3	9
Leghorn . . .	1·028–1·033	1·026–1·027	12	2·90	—
Lodi	1·030–1·034	1·027	12·25	3·50	8·75
Milan	—	—	12·20	3·20	9
Naples . . .	—	—	12	3	9
Palermo . . .	1·029–1·034	1·027	—	3	—
Reggio (Emilio) [1]	1·031	—	12·25	3·25	9
Rome	1·029–1·034	1·027	12	3	9
Turin	—	—	12·50	3·50	9
Venice . . .	—	—	11·50	3	8·5
Verona . . .	—	—	12·50	3·50	9

For a normal *pure milk*, the following mean data may, in general, be accepted :

(a) *Specific gravity at* 15° C.   = 1·0315
(b) *Fat,* %   = 3·50
(c) *Total solids,* %   = 12·25
(d) *Solids not fat,* %   = 8·90
(e) *Specific gravity of the whey at* 15° = 1·027
(f) *Cryoscopic index*   = 0·555°
(g) *Soluble matter,* %   = 6·15
(h) *Refractometric index of the whey* = 39°

Further,

Ash, %   = 0·7–0·8
Lactose, %   = 4·70
Nitrogenous substances, %   = 3–4 (casein 3, albumin 0·5).

Skim milk should contain 1–1·5% of fat, while that containing less than 1% would be *separated milk* ; in either, the solids not fat should be at least 9%, and the specific gravity of the whey 1·027.

[1] Cryoscopic constant, 0·55°.

From the limits given above, it follows :

1. *Addition of water* lowers a, b, c, d, e, g and h, while it brings f nearer to $0°$.

2. *Removal of cream* or *addition of skim milk* raises a, diminishes b and c, and may leave d, e, f, g and h unchanged.

3. *Watering* and *removal of cream together* diminish b, c, d, e, g and h and bring f nearer to $0°$, while a may remain unchanged.

The limits given are, of course, not absolute. Pure milks may be found of somewhat abnormal composition, the latter depending on the period of lactation, the age of the animal and its food, the time of milking (e.g., a cow milked three times a day gives in the evening a milk richer in fat than in the morning), etc. In certain doubtful cases, therefore, it is necessary to compare a suspected milk with milk from the same animals ; in such case the milking must be carried out in the same manner and at the same time, if possible after 24 hours, but never more than 3 days after the suspected milk was obtained.

The extent of adulteration may then be determined by means of various formulæ, in which :

a = added water, in 100 parts of watered milk.

A = water added to 100 parts of pure milk.

s = fat removed from 100 parts of pure milk.

r_1 = percentage of solids not fat in pure milk.

r_2 = percentage of solids not fat in milk considered adulterated.

g_1 = percentage of fat in pure milk.

g_2 = percentage of fat in milk considered adulterated.

l = $100 - a$ = pure milk per 100 of watered milk.

q = quantity of milk considered adulterated.

p_1 = specific gravity of pure milk.

p_2 = specific gravity of milk considered adulterated.

1. *Addition of water.*

This may be calculated by Herz's formula from the solids not fat :

$$a = \frac{100\ (r_1 - r_2)}{r_1}.$$

$$A = \frac{100\ (r_1 - r_2)}{r_2}.$$

It may be calculated also from the fat :

$$a = 100\left(1 - \frac{g}{g_1}\right).$$

Or from the specific gravities :

$$a = q\frac{p_1 - p_2}{p_1 - 1}.$$

The latter formula is equivalent to :

$$a = q\frac{d_1 - d_2}{d_1},$$

where d_1 and d_2 express, for the pure and suspected milks respectively, the indications of the Quevenne lacto-densimeter, that is, the excess of the specific gravity in thousandths above unity.

2. *Removal of cream.*

This may be calculated by means of the following formula :

$$s = g_1 - g_2 + \frac{g_2(g_1 - g_2)}{100}.$$

3. *Watering and removal of cream.*

The removal of cream in watered milk may be calculated by means of the formula :

$$s = g_1 - \frac{\left(100 - \dfrac{gl_1 - 100g}{l}\right)\left(g_1 - \dfrac{lg_1 - 100g_2}{l}\right)}{100}.$$

PRESERVED MILK

Milk is sold preserved in its natural state, i.e. *pasteurised* or *sterilised* and even *frozen* [1]; also *condensed*, with or without addition of sugar, and also in the form of *cakes* and *powder*.

Pasteurised or *sterilised milk* is recognised by the tests already given (p. 29); it has the same composition as natural milk, and should not contain antiseptics or other preservative agents.

Condensed milks are mostly condensed to one-third of their volume. Their composition varies somewhat, according to the degree of concentration and to the addition of sugar (*see* later). Good products should be slightly yellowish, should have no unpleasant smell or cheesy flavour and should be homogeneous and show no clots, fat drops or crystals (lactose).

Condensed milk is usually sold in soldered tins. The analysis should be made immediately after opening, since such products readily change, especially when little or no sugar has been added. Of special importance are tests for antiseptics and other preservatives (*see* Milk, No. 11) and heavy metals, and bacteriological examination.

Milk in cakes or *milk powder* consists of milk reduced by special methods to the dry state: the former often contains added sugar.

Analysis of these products includes the determinations indicated for natural milk and is carried out by the methods already given, the products being well mixed and diluted with water to bring them approximately to the concentration of natural milk (about 12% of dry matter).

With products prepared with addition of sugar, determinations of the saccharose and other sugars, i.e. of the lactose and of the invert sugar which may be formed by the inversion of the saccharose, are carried out by the following methods.

Determination of the Sugars in Condensed Milk.—As soon as the tin is opened, the milk is thoroughly mixed to render it homogeneous and 40 grams [2] weighed in a dish and then washed into a 200 c.c. flask, the dish being washed with boiling water. The solution is diluted to about 180 c.c. with boiling water, heated for a few minutes on a water-bath, treated with 10–15 drops of concentrated acetic acid to coagulate the albuminous substances, shaken for some minutes until the coagulum separates well and then cooled rapidly. Next, 10 c.c. of basic lead acetate solution are added and, after a quarter of an hour, 20 c.c. of saturated sodium sulphate solution. The solution is then made up to the mark with cold water and 4 c.c. of water added to compensate for the volume of the precipitate [3]; the whole is well shaken, allowed to deposit and filtered through a pleated filter.

[1] With frozen milk it should be borne in mind that the analysis must be made on a sample representing the whole mass; otherwise the results may be quite erroneous.

[2] For milk in cakes or powder, 20 grams suffice, this being allowed for in the calculations, which in the text are given for 40 grams of substance.

[3] The amount of water indicated represents the mean of numerous determinations made on many samples of condensed milk and is accurate in most cases.

With condensed milks containing much fat (not de-creamed) it may be useful to verify the volume occupied by the coagulum. To this end 40 grams and 20 grams of the milk are treated as above in two 200 c.c. flasks, the indicated amounts of basic

The *filtrate* serves for the different determinations as indicated below. The polarisation before and after inversion is determined, and also the reducing power. From the two polarisations the saccharose is calculated according to Clerget's method ; the saccharose is also calculated by Girard's method, i.e. from the polarisation found directly, diminished by that due to the reducing sugar calculated as lactose. If the results obtained by the two methods are concordant, no invert sugar is present and the percentage of lactose is taken as that calculated from the reducing power. In the contrary case, invert sugar is present ; the percentage of saccharose is then taken as that found by Clerget's method, and the lactose and invert sugar are calculated, by means of a series of equations, from the direct polarisation (diminished by that due to the saccharose) and the reducing power.

The method of procedure and calculation are as follows :

1. DETERMINATION OF THE SACCHAROSE BY INVERSION. (*a*) 50 c.c. of the *filtrate* are made up to 100 c.c.[1] and the liquid read directly in a 20 cm. tube in a saccharimeter with a Ventzke scale. Multiplication of the reading by 2 gives P, the polarisation of the filtrate.

(*b*) Another volume of 50 c.c. of the *filtrate* is heated in a 100 c.c. flask with 5 c.c. of hydrochloric acid (D 1·10) for 15 minutes in a water-bath at 68–70° to invert the saccharose, the liquid being then cooled, neutralised with 30% caustic soda (towards phenolphthalein), made up to 100 c.c. and read in the saccharimeter in a 20 cm. tube, the exact temperature of the liquid being noted. Multiplication of the reading by 2 gives P_1, the polarisation of the original liquid after inversion.

The percentage, S, of saccharose in the condensed milk is given by the Clerget formula,[2]

$$(\text{I}) \qquad\qquad S = 5 \frac{26 \cdot 048 \ (P - P_1)}{142 \cdot 66 - 0 \cdot 5 \, t}.$$

2. DETERMINATION OF THE LACTOSE AND SACCHAROSE BY GIRARD'S METHOD. (*a*) In a part of the *filtrate* which has been used for the direct reading of the saccharimeter according to 1 (*a*), the lactose is determined by means of Fehling's solution (50 c.c. diluted with 200 c.c. of water), boiling for 6 minutes.[3]

lead acetate and sodium sulphate being added and the liquids made up to the mark and filtered. The filtrates are read in the polarimeter in 20 cm. tubes. If the readings are *a* and *b* for the 40 and 20 gram solutions, the volume *v* of the insoluble substances (coagulum) contained in 20 grams of milk will be :

$$v = 100 \ \frac{(a - 2b)}{(a - b)},$$

and 2*v* will be the number of c.c. of water to be added in excess to the solution of 40 grams of the milk made up to 200 c.c.

If various samples of milk of the same type are to be analysed, the correction calculated in this way may be applied in each case.

[1] The formulæ which follow hold when vessels graduated in Mohr c.c. (*see* Chapter on Sugars) are used.

[2] In this formula no account is taken of the variation of the rotatory power with the concentration ; when this is desired, the procedure is as indicated in the Chapter on Sugars.

[3] 10 c.c. of Fehling solution and 40 c.c. of water may be used, as indicated for sugars (General Methods) and milk (8) ; if, then, *a* is the number of c.c. of the diluted solution necessary to decolorise the 10 c.c. of Fehling solution used, 5 *a* should be inserted in formula (II) in place of *a*.

If n is the total dilution to which the original filtrate is subjected to obtain the solution used in the Fehling titration, and a the number of c.c. of the diluted solution required to decolorise the 50 c.c. of Fehling solution, the *lactose* (hydrated) L contained in 100 grams of the milk analysed is given by the formula:

(II)
$$L = \frac{676\,n}{4\,a}.$$

(b) From the lactose thus found, the polarisation due to it is calculated by dividing by 0·3295 (grams of lactose in 100 c.c. which rotate 1° Ventzke). Deduction of this polarisation from the direct polarisation P of the original liquid (*see* I, *a* above), multiplied by 5 gives the polarisation due to the saccharose present alone; from this the saccharose is calculated, knowing that 1° Ventzke corresponds with 0·26048 gram of saccharose per 100 c.c. Hence the percentage of *saccharose* is given by the formula [1]:

(III)
$$S = 0·26048 \left(5\,P - \frac{L}{0·3295} \right).$$

3. DETERMINATION OF LACTOSE AND INVERT SUGAR PRESENT TOGETHER. If invert sugar is present in appreciable quantity (as happens sometimes if the milk has not kept well), the percentage of saccharose is determined by the Clerget method (*see* above, formula I *a*). The polarisation R due to the lactose and invert sugar is then calculated by subtracting the rotation due to the saccharose (which is obtained by multiplying the percentage of saccharose by 3·839) from five times the initial rotation P of the original liquid (*see* I, *a*).

From the data of the Fehling titration (*see* 2, *a*), the number of c.c. F of Fehling solution which would be reduced by the total reducing sugars present in 100 grams of milk is calculated by means of the formula [2]:

$$F = \frac{25000\,n}{a}.$$

This done, these data are introduced into the equations:

$$3·035\,x - 1·191\,y = R$$
$$148\,x + 194\,y = F,$$

in which x is the percentage of *lactose* and y that of *invert sugar*. These equations give:

(IV)
$$x = \frac{194\,R + 1·191\,F}{765}.$$

(V)
$$y = \frac{3·035\,F - 148\,R}{765}.$$

EXAMPLE: 40 grams of condensed milk, dissolved and made up to 204

[1] These calculations may be shortened by using tables compiled by Vaccaroni (*Annali Lab. chim. Gabelle*, 1914, VII, 253).

[2] If 10 c.c. of Fehling solution were used in the titration instead of 50 c.c., a in the formula should be replaced by 5 a.

c.c. after addition of acetic acid, lead acetate and sodium sulphate gave a liquid which, when filtered and diluted to double its volume, gave (1, a):

$$P = + 37 \cdot 6.$$

The inverted liquid, read in the polarimeter according to 1, b, gave:

$$P_1 = -3 \text{ at } t = 12 \cdot 5°.$$

With the remainder of the liquid used for the polarisation according to 1, a (dilution $n = 2$), the Fehling titration is carried out as in 2, a:

$$a = 25 \cdot 5 \text{ c.c.}$$

From these data are calculated:

The saccharose by Clerget's formula (I), introducing the values of P, P_1 and t. Thus,

$$S = \frac{26 \cdot 048(+ 37 \cdot 6 + 3)}{142 \cdot 66 - 0 \cdot 5 \times 12 \cdot 5} \times 5 = 38 \cdot 76\%.$$

The lactose (assuming absence of invert sugar) by formula (II), into which the value of a is introduced. Thus,

$$L = \frac{676 \times 2}{4 \times 25 \cdot 5} = 13 \cdot 25\%.$$

The saccharose, according to Girard, by formula (III), the above value of P and the value of L just found, being inserted:

$$S = 0 \cdot 26048 \left(5 \times 37 \cdot 6 - \frac{13 \cdot 25}{0 \cdot 3295} \right) = 38 \cdot 50\%.$$

If, however, the presence of invert sugar in appreciable amount is assumed, the lactose x and the invert sugar y are calculated from formulæ (IV) and (V), inserting in these the values:

$$R = 37 \cdot 6 \times 5 - 38 \cdot 76 \times 3 \cdot 839 = 39 \cdot 2$$

$$F = \frac{25000 \times 2}{25 \cdot 5} = 1960 \cdot 8$$

Thus,

$$x = \frac{194 \times 39 \cdot 2 + 1 \cdot 191 \times 1960 \cdot 8}{765} = 12 \cdot 99\%$$

$$y = \frac{3 \cdot 035 \times 1960 \cdot 8 - 148 \times 39 \cdot 2}{765} = 0 \cdot 20\%.$$

The milk examined thus contains invert sugar and this explains why the Girard method does not give results for the lactose and saccharose identical with those obtained by the other methods. In such a case the value for the saccharose is to be taken as that found by the Clerget formula, so that the milk contains:

Saccharose	38·76%
Lactose	12·99
Invert sugar	0·20

As a rule milks which have been well prepared contain either no invert sugar or but very little.

BUTTER

This is the fat of milk, separated from the other components, but containing incorporated in it a certain quantity of curd: it is semi-pasty, white or pale yellow, with agreeable odour and taste, and turns rancid easily.

Butter is adulterated principally with oleomargarine [1] and less frequently with other animal or vegetable fats (tallow, cacao-butter, cotton-seed stearine, oils) ; sometimes considerable quantities of water are incorporated with it and preservatives (ordinary salt, borax or boric acid, salicylic acid, formalin, fluorides or fluoborates, etc.) or colouring matters added ; very rare are such coarse adulterations as gypsum, chalk, flour, glucose, sodium silicate, etc.

The more important tests and determinations to be made are those described in 1, 2, 3, 4, 11, 12 and 15, which are usually sufficient to indicate if a butter is genuine ; if a more complete analysis is desired, the other tests described may be carried out. Where not otherwise indicated, the tests are to be made on the fused and filtered butter fat.

1. Volatile Acid Number.—The volatile acid number or the Reichert-Meissl number denotes the number of c.c. of N/10-alkali required to neutralise the volatile acids, soluble in water, obtained from 5 grams of butter fat, previously melted and filtered. It is determined exactly as described in the chapter headed Fatty Substances (Vol. I, p. 377).

The Italian Official Method (1905) is the Reichert-Meissl-Wollny method with Leffmann and Beam's modifications (see observations relating to this method in the chapter on Fatty Substances, Vol. I, p. 378).

Owing to its high content in glycerides of volatile acids, butter fat gives a very high volatile acid number, while other animal fats and also most vegetable oils give very low values—rarely more than 1—with the exception of coconut oil, for which the value is about 7–9.

The presence in butter of salicylic or benzoic acid in greater proportion than is generally used as preservative (0·1–0·2%) raises the volatile acid index. [2]

2. Butyro-refractometer Reading.—The Zeiss butyro-refractometer, here described (see Fig. 6), is a modification of the ordinary Abbé refracto-
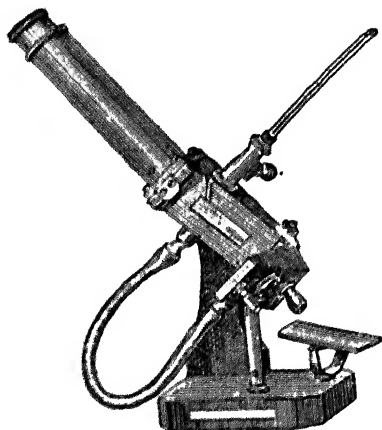
Fig. 6

meter, provided with an arrangement for heating by passing a current of hot water round the prisms between which the fat to be examined is placed. The eye-piece tube contains a special micrometer scale divided into 100 parts, the zero corresponding with the refractive index, 1·4220; and the 100 point with the index 1·4895 ; the divisions are termed *refractometric degrees*. The scale is rendered movable in the field of the apparatus by means of a drum, and by means of the micrometer screw of the latter the tenths of the scale divisions may be determined.

The prisms of this instrument are achromatised so as to render the limiting line of total reflection, that is, the line separating the illuminated

[1] See articles on Oleomargarine (Vol. I, Fatty Substances) and Artificial Butter (this chapter).

[2] Grimaldi : *Annali Labor. Cent. delle Gabelle*, Vol. VI, p. 631.

from the dark field (observed in the instrument in presence of a fatty substance), perfectly clear and colourless in the case of butter. With fats having a dispersive power different from that of butter, the illuminated field exhibits coloured fringes and the boundary line appears blue or red according as the dispersion is greater or less than that of butter.

To make an observation, the two contiguous prisms of the apparatus are removed and the free surfaces cleaned with a soft cloth moistened with alcohol and ether. Two or three drops of the fused and filtered fat are then dropped on to the surface of one of the prisms (the instrument being inclined so that the surface of the movable prism is horizontal), the prisms being brought into perfect contact again. A current of water at 35°, from a reservoir holding at least 10 litres and previously heated, is next passed round the prisms. The position of the mirror at the base of the instrument is then adjusted so that the line separating the light from the dark half of the field (line of extinction) is distinctly seen.

It is made certain that the fused fat fills regularly and entirely the narrow space separating the two prisms, this being done by observing with the naked eye or with a lens the small rectangular image of the surface of the prism seen about 1 cm. above the eye-piece.

The line of extinction, now observed through the eye-piece, is at first indefinite, but when the temperature of the apparatus has remained constant at 35° for some minutes, it appears quite fixed and sharp. Note is then made of the division of the scale with which the line of extinction coincides and if this line is colourless or coloured. The division of the scale, thus read, is the *refractometric degree*.

From time to time, it is necessary to verify the accuracy of the scale by placing between the prisms three or four drops of the *normal liquid* supplied, together with the values of its refraction at different temperatures, with each apparatus.

If the temperature differs from 35°, a correction may, within a few degrees, be made ; this correction amounts to 0·55 per degree of temperature and is added or subtracted according as the reading is taken above or below 35°. Thus, a butter giving a reading of 44 at 40° would give a reading of $44 + (0.55 \times 5) = 46.75$ at 35°.

3. Microscopic Examination in Polarised Light.—This is carried out with a microscope furnished with a polarising apparatus, a plate of selenite about 0·2 mm. in thickness being fitted on the diaphragm of the microscope and hence below the preparation. The magnification should be 150–170 diameters.

The analysing prism is first placed at right angles to the polarising prism, so that the field appears green ; the analyser is then rotated through 90°, the field then appearing red with a violet shade.

The preparation is made by squeezing a piece of butter not larger than a pea between two microscope slides so that the interposed fat makes the glasses clear. This is then observed in the microscope arranged to give the red field.

With pure butter, which has not been previously melted, no change of tint is observed, but only darker granulations on the red ground. Salt

butter behaves similarly, excepting that, when crystals of salt are in the field, the light at the corresponding places is brighter although of the same colour.

Melted butter gives a field interspersed with shining, iridescent, irregular or radiating groups, reflecting all the colours of the spectrum, yellow, green and blue predominating.

Oleomargarine behaves like melted butter.

Mixtures of butter and margarine give a brown field with shining points of different colours, the number of these increasing with the proportion of margarine.

4. Specific Gravity.—Determined at 100° as in fatty substances (Vol. I, p. 371).

5. Water. Between 5 and 10 grams of the butter, weighed in a porcelain or platinum dish, are kept at 100–105° for 6 hours, the dish being cooled in a desiccator and reweighed ; loss in weight gives the water.

6. Ash. 10 grams of the butter are incinerated carefully and at a low temperature in a porcelain or platinum dish, the ash being weighed when cold. The residue from 5 (above) may be used in this test.

In the Italian Official Methods (1905), the determination of ash is preceded by that of *solids not fat*, free from water. The residue from the estimation of water (*see* 5) is treated with absolute alcohol and ether, the insoluble remainder being collected on a tared filter, dried and weighed ; this gives the *non fat*. This filter is then incinerated and the weight of the ash thus found.

7. Sodium Chloride.—The weighed ash is dissolved in water, the solution made up to a definite volume and filtered, and an aliquot part used for the volumetric or gravimetric estimation of the chlorine.

8. Fat.

    (*a*) By Gerber's Acido-Butyrometer. In this case the butyrometer with two apertures (Fig. 7) is employed. At the lower stopper is inserted a beaker containing a weighed quantity of 4–5 grams of the butter, well mixed. The small aperture is closed, the butyrometer inverted and 10 c.c. of sulphuric acid (D 1·820–1·825 at 15°, as for milk) and then 10 c.c. of distilled water and 1 c.c. of amyl alcohol added ; the large aperture is next closed with the stopper carrying the beaker so that this remains within the butyrometer. The latter is immersed in a water-bath at 50–55° and when the butter is melted it is stirred slowly to dissolve the curd ; the instrument is then placed in the water-bath again for a few minutes, centrifuged, immersed in the bath at 65° once more and the reading taken.

The percentage of fat is given by the formula :

$$F = \frac{5 \times n}{p} - 0.5,$$

where n is the number of the line read on the butyrometer, p the quantity of butter weighed out, and 0·5 represents a mean positive error of the method

    (*b*) By Direct Extraction. 10 grams of butter, mixed with pumice and dried, are exhausted with anhydrous ether either in an extraction

apparatus for about 12 hours or by direct heating, the ethereal solution being decanted on to a pleated filter, through which it passes into a tared flask, the filter being well washed with ether into the same flask. The ethereal solution is distilled at a low temperature and the flask and fatty residue dried in a steam-oven to constant weight.

The fat in butter may also be determined *indirectly* by subtracting from 100 the sum of the water (*see* 5) and the non-fatty residue (*see* 6), but this method is less accurate than the two given above.

9. Saponification Number.—This is determined on the butter fat in the way indicated in the chapter on Fatty Substances (Vol. I, p. 375).

10. Iodine Number.—Determined on the butter fat as indicated in the chapter on Fatty Substances (Vol. I, p. 379).

11. Preservatives and Antiseptics.

The more common of these are tested for as follows:

(*a*) BORIC ACID AND BORATES. The procedure is as with milk (*see* Milk, 11, *a*), 10 grams of the butter being incinerated.

For a quantitative estimation, 10–20 grams of the butter are charred in presence of sodium carbonate, the residue being dissolved in water and the solution made up to a given volume; the subsequent procedure is as with meat (*see* Chapter I, p. 7).

(*b*) SALICYLIC ACID AND SALICYLATES. About 20 grams of the butter are well shaken in the hot with 10% sodium bicarbonate solution; the aqueous liquid is separated, acidified with dilute sulphuric acid and extracted with a mixture in equal volumes of ether and petroleum ether. The ethereal liquid is separated and evaporated, the residue being tested for salicylic acid as indicated for milk (11, *a*).

(*c*) BENZOIC ACID, FORMALDEHYDE, FLUORIDES, FLUOBORATES. The methods given for milk are applied either to the butter itself or to the aqueous liquid separating from it on melting (*see* Milk, 11).

12. Various Extraneous Matters.—From 10 to 20 grams of the butter are boiled with water, the aqueous liquid being filtered and tested by the usual analytical methods for alum, borax, sodium silicate, sugar and glucose.

Another quantity of 10–20 grams is treated with ether and filtered, the insoluble part being well washed with ether. If there is much insoluble matter, it is tested for starch microscopically and for gypsum, chalk, etc., by the ordinary analytical methods.

13. Colouring Matters.—In Italy butter may be coloured, but not with certain prohibited colouring matters, such as Martius yellow, Victoria yellow and metanil yellow. As a rule annatto is used, but sometimes also saffron or turmeric, and rarely carotin; coal-tar colours (aniline yellow, butter yellow) are also employed.

Natural butter, dissolved in petroleum ether and treated in the hot with ethyl or methyl alcohol, gives solutions scarcely coloured a faint straw yellow; if artificial colour is present, the solutions are more or less intense yellow.

TABLE II

Distinctive Reactions for Butter Colouring Matters

	Conc. Sulphuric Acid.	Conc. Nitric Acid.	Conc. Hydrochloric Acid.
Butter alone	Reddish to crimson	The yellow residue assumes a brownish-yellow tone	At first no change; on standing sometimes a faint red colour
With annatto	Green, blue and, slowly, violet	Transient blue, becoming pale green and then colourless	The yellow residue assumes an orange tint
With turmeric [1]	Violet-red	Violet-red, somewhat transient	Violet-red; on evaporating the acid, brownish colour turning violet on addition of acid
With saffron	Dark blue, rapidly becoming violet-red and then reddish-brown	Blue, immediately becoming green and then reddish	The residue assumes only a browner tone
With carotin	Violet-brown to purple, gradually changing to violet and brown	Dark yellow and then pale yellow	Light brown
With Martius yellow	Yellow becoming reddish	Yellow with separation of reddish droplets	Yellow, then yellow precipitate turned orange by ammonia
With Victoria yellow	Brown colour, turned canary yellow by ammonia	As with sulphuric acid	Decolorised, but becomes yellow again on addition of ammonia
With Metanil yellow	Crimson [2]	Crimson, soon changing to violet-red	Crimson
With Aniline yellow	No change	No change	No change
With Soudan yellow	Crimson, more or less intense [3]	Crimson	Red
With Butter yellow (dimethylaminoazobenzene)	Red, changing at once to yellow and then to red again on dilution with water	Crimson	Crimson

[1] With ammonia the residue gives a reddish-brown coloration; evaporation of the ammonia leaves a yellowish-brown residue, which becomes violet with hydrochloric acid.

[2] Crimson even when the respective dilute acids used are greatly diluted.

[3] Red even with the dilute acids.

To investigate the colouring matter added,[1] 15–20 grams of the butter are boiled in a reflux apparatus with about 40 c.c. of methyl alcohol. When thoroughly cold (best in ice) the liquid is filtered and to the residue from a few drops of the alcoholic solution evaporated in a porcelain capsule is added, drop by drop down the side of the dish, conc. sulphuric, nitric or hydrochloric acid, the colour manifested being observed.

The behaviour of the residue from pure butter and of butter coloured with various colouring matters is shown in Table II.

14. Vegetable Oils.—The adulteration of a butter with vegetable oils, or rather with substitutes containing vegetable oils, may be detected by the usual colour reactions, especially those serving to characterise sesamé oil (Villavecchia and Fabris' reagent), cottonseed oil (Halphen's reagent), and arachis oil (*see* Fatty Substances). The test for phytosterol may also be made as indicated in the chapter on Fatty Substances (Hog's Fat, Vol. I, p. 423).

15. Cacao Butter.—Use is made of Polenske's method, according to which the number of c.c. of N/10-alkali required to neutralise the insoluble volatile acids is determined (*Polenske number, Insoluble volatile acid number, New butter number*). This number may be determined directly or indirectly.

(*a*) DIRECTLY. From 5 grams of the butter fat the volatile acids are separated as indicated in Vol. I, p. 377, but the distillation is carried out more rapidly, so that 110 c.c. are collected in about 20 minutes and the temperature of the distillate is about 20–23°. The flask, with the 110 c.c. of distillate, is immersed for about 15 minutes in cold water and then filtered through a filter-paper 8 cm. in diameter.

The filtrate serves, as usual, for the determination of the soluble acids, whilst the insoluble volatile acids collected on the filter (if these are liquid the presence of cacao butter is highly probable) are washed three times with 15 c.c. of distilled water, which is previously used each time to wash the tube of the condenser and the flask. These three washings are usually sufficient to remove all the soluble volatile acids ; if the last 10 c.c. of wash water are not neutralised by a drop of N/10-alkali, a fourth washing is carried out.

The washing of the condenser and filter is then repeated three times with 15 c.c. each time of 90% alcohol and the alcoholic solution of the insoluble fatty acids, collected in the flask, titrated with N/10-alkali in presence of phenolphthalein : the number of c.c. of alkali required represents the insoluble volatile acid number.

(*b*) INDIRECTLY. The volatile acid number bears a certain relation to the insoluble volatile acid number, so that the latter may be calculated from the former by multiplying by either 0·7 or 0·5 according as the value (of the former) is less than or greater than 27.

The following table gives the results of such calculation for genuine butters :

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[1] A. Bianchi : *Annali di Chim. Applicata*, 1916, **V**, p. 1.

Volatile Acid Number.	Insoluble Volatile Acid Number.	
	Extreme Normal Limits.	Maximum allowable.
20–21	1·3–1·4	1·9
21–22	1·4–1·5	2·0
22–23	1·5–1·6	2·1
23–24	1·6–1·7	2·2
24–25	1·7–1·8	2·3
25–26	1·8–1·9	2·4
26–27	1·9–2·0	2·5
27–28	2·0–2·2	2·7
28–29	2·2–2·5	3·0
29–30	2·5–3·0	3·5

Addition of cacao butter to butter raises the insoluble volatile acid number in proportion to the extent of the addition :

Percentage of Cacao Butter added.	Mean increase of the Insoluble Volatile Acid Number.
10	1·00 (0·8–1·2)
15	1·80 (1·4–1·8)
20	1·90 (1·9–2·2)

The Italian Official Methods (1905) give Muntz and Coudon's method, based on the different values of the ratio existing between the soluble and insoluble volatile acids, calculated as butyric acid, in cacao butter and in butter :

$$\frac{\text{Insoluble acids}}{\text{Soluble acids}} \times 100 = 10\text{–}15 \text{ for butter and} = 250\text{–}280 \text{ for cacao butter.}$$

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As the composition of *natural butter* varies with the region, breed, individual, food, etc., it is difficult to fix absolute mean or limiting values, so that the data obtained must be referred to those of genuine butters of the same region and period. When the origin is unknown, it is possible to give a definite judgment for certain determinations (percentages of fat, water and ash, specific gravity, refractive index), but care should be exercised in cases where the tests fail to give affirmative and concordant results. It should be borne in mind that butter of abnormal composition is an exception and generally arises from a poor condition of the animal, caused by faulty nutrition or disease.

Butter melts at 30–40° to a yellow, oily liquid termed *butter fat*, floating on a little turbid aqueous liquid containing a small amount of coagulated albuminoids. With the ordinary solvents (ether, benzene, etc.) it gives turbid solutions, and with the usual reagents for oils it gives no appreciable colour reactions unless it is rancid. It consists of butter fat, together with a certain quantity of non-fatty substances (water, albuminoids, milk sugar, salts), which may amount to 15–16% of the butter, but in good butters are more generally about 12%.

The physical and chemical characters of butter fat mostly lie within the following limits :

Density at 98–100°	0·865–0·868
Melting point	28–36°
Solidifying point	19–23°
Melting point of the insoluble fatty acids	38–45°
Solidifying point of the insoluble fatty acids	33–38°

Acid number : fresh butter contains very small quantities of free acids (less than 0·5%), but as it readily turns rancid it may soon assume a higher degree of acidity.

Saponification number = 220–232. A very low saponification number may indicate the presence of other fatty substances, the saponification number of which is usually 195–200 ; a very high number may denote the presence of cacao butter, which mostly has the saponification number, 250–265.

Iodine number = 26–40.

Fixed acid number (Hehner) = 85–91.

Volatile acid number (Reichert) = 25–30, exceptionally 33. That for cacao butter = 7 – 9, and that for vegetable oils and animal fats about 1 or rather more.

Insoluble volatile acid number (Polenske) = 2·20–3·00 (*see* Table under 15, p. 42).

Refractive index = 41–45 (at 40°), 44·5–46·5 (at 35°) and sometimes 47·5.

The regulation passed (in Italy) in 1894 defines the conclusions to be drawn from certain of the estimations mentioned above. Thus, as regards the *volatile acid number* : butters the fat of which requires not less than 26 c.c. of N/10-alkali are to be regarded as genuine, when there are no contrary indications ; less than 20 c.c. indicates *adulteration* ; values between 20 and 26 are *suspicious*, when the other data (age of the butter, season of the year, etc.) do not permit of a decision. In such a case it is advisable, where possible, to examine a genuine sample of butter from the same source, provided that this can be obtained shortly after the suspected butter.

Butter giving a *butyro-refractometer* reading higher than 48 at 35° may, without further test, be taken as *adulterated*. Also recently made butter which, in *polarised light*, shows a crystalline structure, is to be regarded as adulterated ; if the butter is not known to be of recent preparation, the crystalline structure renders it *suspicious*. Further, butter having at 100° a lower *specific gravity* than 0·865, with reference to water at 15°, is to be taken as *adulterated*.

The mean composition of butter is as follows :

TABLE III

Mean Percentage Composition of Butters

Quality.	Water.	Fat.	Albuminoids.	Lactose and Lactic Acid.	Ash.
Good . . .	12·20	87·00	0·30	0·40	0·10
Medium . .	16·00	82·75	0·53	0·60	0·12

SKIM MILK BUTTER

In addition to cream butter, a poorer product, *skim milk butter,* is made from the cream, separated either spontaneously or mechanically, of the residual whey from the manufacture of cheese. It is recognised mainly by its low percentage of dry solids not fat which scarcely amounts to 0·5.

Sometimes, however, the cream is separated by heating the acid whey and then the proportion of non-fatty solids may reach 2%, owing to the large amount of albuminoids it contains. According to Fascetti, such butter may be recognised as follows : an alcoholic solution of roccellin (0·5

gram in 150 c.c. of 65% alcohol) is incorporated drop by drop with 2 grams of butter so that the paste assumes a uniform red coloration. Under the microscope this paste appears colourless if from fresh butter or pure cream, but exhibits bright red spots if from reheated butter, owing to the intense fixation of the colouring matter by the flocks of the albumin. This test assumes that, during washing, the butter has not been deprived of the caseo-albuminous residues derived from the cream used in its preparation.

ARTIFICIAL BUTTER

Artificial butter is commonly obtained by emulsifying oleomargarine with skim milk, usually with the addition of varying proportion of vegetable oils (sesamé, arachis, cottonseed), animal fats (beef fat, neutral hog's fat), aromatic substances (ethyl butyrate, coumarin), and sometimes also casein, lactose and egg-yolk; in some cases it is artificially coloured (annatto, coal-tar colours).

It is usually sold under the name *margarine*, and it has the appearance and consistency of ordinary butter and pleasing external characters, but with practice it is readily distinguishable from real butter.

The physical and chemical characters of margarine, after melting and filtering, are naturally related to the fatty substances used in its preparation. For its analysis, use is made of the methods indicated for the various oils and fats (*see* Fatty Substances, Vol. I), and its distinction from butter is effected by the methods described for butter. Further, the methods there given are used for testing for various extraneous matters (flour, mineral substances), preservatives (salicylic acid, boric acid, etc.) and colouring matters.

To distinguish margarine from oleomargarine it is sufficient to heat a portion in a test-tube; the former gives a turbid liquid almost like natural butter, whilst oleomargarine yields a perfectly clear liquid. Further, if oleomargarine is heated for some hours at 100–105° it does not lose sensibly in weight, whilst margarine loses 10–16%.

Besides margarine, there are other artificial butters in which the oleomargarine is substituted, partly or wholly, by cacao butter; for these, too, the general methods for the analysis of fatty substances (*see* Vol. I) and especially those given for butter are employed.

CHEESE

This is formed of the nitrogenous substances (casein, albumin) and fats contained in milk, separated by coagulation (by rennet or by acidification). As a result of special fermentations which occur during the *maturation* of the cheese, these give rise to soluble albuminoid substances (albumoses, peptones, etc.), amino-acids (phenylaminopropionic acid, tyrosine, leucine, etc.), ammoniacal products, fatty acids (lactic, propionic, caproic), etc. Cheese also contains water and mineral salts, including added sodium chloride.

The examination of cheese comprises essentially: the observation of

the objective characters ; the quantitative determination of the chief components, namely, water, nitrogenous substances, ash, fat ; tests for heavy metals or other extraneous substances, to ascertain if the cheese has undergone change or is harmful ; determination of the nature of the fat present to decide on the origin of the cheese (pure, margarine, cacao butter).[1] These tests and determinations are described below.

Sampling.—The sample is taken by means of a tester, which is introduced in different parts of the cheese if this is a large one. With small cheeses, the whole of one or even more than one is taken, the dirt and rind being removed. Hard cheese is powdered by rasping, while soft cheese is pounded in a mortar.

1. External Characters.—The cheese is struck with the knuckle or with a small hammer on the rind to ascertain if it gives a clear, sharp sound (sound cheese) or if there is discontinuity (blisters, honey-combing, fissures). The interior is examined to ascertain if this is homogeneous, and in the case of a cheese with cavities, if these are uniform ; to determine if the odour is agreeable and piquant (sound cheese) or repulsive (altered), if the taste is that characteristic of the particular cheese and if the colour is uniform or if red, black or bluish spots are present.

2. Water.—5 grams of the cheese (if soft, mixed with 20 grams of calcined coarse sand) are dried, first in a vacuum over sulphuric acid and then in an oven at 100° to constant weight ; the loss represents water.

Besides water, other volatile substances may be lost, such as ammonia and any other decomposition products in the cheese, although these are usually in negligibly small proportion.[2]

3. Fat.—This may be determined volumetrically or gravimetrically.

(a) VOLUMETRICALLY. Siegfeld's modified method of using Gerber's acido-butyrometer is followed. A weight of 2·5 grams of the cheese is heated in a flask with 10 c.c. of sulphuric acid (D = 1·5–1·6) in a water-bath at 70–80° with frequent shaking until dissolved. The whole is then introduced into a Gerber butyrometer for cheese (Fig. 8)—which is very similar to that used for butter—and the flask washed out with a further quantity of sulphuric acid so that 20 c.c. in all are taken. According as the cheese is fat or lean, 0·5 or 1 c.c. of pure amyl alcohol is added. The butyrometer is then closed, shaken, placed in a water-bath at 65–70° for some minutes and shaken at intervals ; it is next centrifuged for 5 minutes, immersed again in the bath for a few minutes, once more centrifuged and the layer of fat read off at the temperature of the bath. The reading is corrected by an amount varying from 0·1 for readings of 4–11 to 0·6 for readings of 37–40.

FIG. 8

The method gives good results with fat cheeses, but not so good with lean cheeses, for which the gravimetric methods described later are advisable. The Gerber method, without Siegfeld's modifications—the cheese being weighed directly in the beaker inserted in the

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[1] In addition to the tests and determinations described below, a bacteriological investigation may also be made.

[2] If the cheese contains estimable quantities of ammonia, this may be determined separately and then deducted from the loss in weight at 100°.

stopper of the butyrometer—is given in the Italian Official Methods (1905), with the proviso that the correction to be applied to the reading is equal to that already indicated for the same method with butter (*see* Butter, 8).

(*b*) GRAVIMETRICALLY. One or other of the following is used:

1. In a mortar containing a considerable amount of calcined coarse sand or pumice are placed 3–5 grams of the cheese, the whole being maintained for some hours in an oven at about 100°, or better in a vacuum over sulphuric acid. The cheese is then well pounded with the sand and the mixture placed in a paper thimble and extracted with anhydrous ether in an extraction apparatus for 4 hours. The residue is subsequently pounded again and extracted anew for 2 hours with fresh ether. The united ethereal solutions are distilled and the residue dried for an hour at 100° and weighed.

The fat extracted is accompanied by the lactic acid when this is present in the cheese; in such case it is well previously to neutralise the acid with sodium carbonate.

2. Schmid and Bondzynski's method : From 3 to 5 grams of the finely divided cheese are heated in a flask over a flame with 10 c.c. of hydrochloric acid (D = 1·125) until the casein dissolves, the solution being transferred to a graduated 100 c.c. cylinder and the flask rinsed out several times with ether (25 c.c. in all), which is also poured into the cylinder. After thorough shaking, 25 c.c. of petroleum ether are added, the whole being shaken again and treated as with milk (*see* Milk, 5, *b*).

These two methods give good results also for lean cheeses, the second being the more rapid.

4. Determination of the Nitrogenous Substances.—These are determined by the Kjeldahl method, using 1–2 grams of the cheese and 25 c.c. of phosphoric-sulphuric acid : Nitrogen × 6·37 = nitrogenous substances.

5. Soluble Nitrogenous Substances.—This determination aims more particularly at establishing the degree of maturation of the cheese, and is made as follows : 20 grams of the sample are dried at about 40° and then extracted with ether to remove the fat. 10 grams of the fat-free residue are pulped with water to a fluid paste, which is treated in a 500 c.c. measuring flask with about 400 c.c. of water, being shaken from time to time during 15 hours at the ordinary temperature ; a drop of formaldehyde is added to prevent putrefaction. The liquid is subsequently made up to volume, mixed and filtered, 100 c.c. of the filtrate (= 2 grams of substance) being evaporated to dryness in a Kjeldahl flask and the residue treated as usual by the Kjeldahl method.

6. Acidity.—10 grams of the cheese are repeatedly heated with water, which is decanted off after each treatment. The whole liquid is filtered and made up to 200 c.c., 100 c.c. (= 5 grams of substance) being titrated with N/10-potash in presence of phenolphthalein. The acidity is calculated as lactic acid : 1 c.c. N/- potash = 0·009 gram of lactic acid.

7. Ash.—5 grams of the cheese are carefully charred in a platinum dish, the carbon being powdered and then burnt at a dull red heat or, better, lixiviated with water and treated as indicated for milk (*see*, Milk, 8).

The ash may be used for the determination of the sodium chloride and for testing for heavy metals (especially copper and lead), barium and talc ; with soft cheeses, the two latter may arise by infiltration from the artificial layer coating the rind.

8. Nature of the Fat.—From 100 to 200 grams of the cheese, free from rind and finely grated, if hard, or made into a paste with sand, if soft, are pulped in a mortar with water heated to about 35°, with repeated agitation to allow the casein to swell and liberate the fat.   As soon as the mass begins to become buttery, it is poured into a 500 c.c. flask, the mortar being washed out with distilled water at 20° in amount equal to 2½ volumes per 1 volume of cheese.   The whole is shaken and after about 5 minutes the butter separates at the surface in clots which, by a gentle movement, may be collected into a single mass.   The latter is then brought into the neck of the flask by addition of cold water and transferred by means of a spoon into a beaker, in which it is washed twice with water.   It is then dissolved in 200 c.c. of petroleum ether (b.pt. 50°) or anhydrous ether, the ethereal solution being left at rest for a couple of hours or so in a cylinder with a ground stopper.   From 100 to 150 c.c. of the ethereal solution are decanted off or, if still turbid, filtered, and evaporated slowly on a water-bath until the whole of the ether is expelled.   The fat thus obtained is analysed, determinations being made especially of the volatile acid number, the refractometric reading, and possibly the saponification number, specific gravity, Polenske number, etc., as indicated for butter (*q.v.*).

To decide if it consists of true milk fat or of margarine or mixtures, and thus if the cheese has been made from milk alone or from margarine or other fats, the criteria used for butter serve.

This procedure is indicated in the Official Italian Methods (1905).   The fat may, however, be extracted by the other methods given for the gravimetric estimation of the fat (*see* especially, 3, *b*, 1), a larger quantity of the sample—at least 100 grams—being taken.

9. Colouring Matter.—Cheese is coloured with annatto, saffron (especially in Italy), or coal-tar colours.   These are detected as in butter (*see* Butter, 13).

10. Various Extraneous Substances.—Cheese is sometimes, although rarely, adulterated with flour or starch, recognisable microscopically ; it should be noted that some special cheeses (e.g. Roquefort) are prepared with the addition of mouldy bread crumb, etc.

11. Cheese Poison (*Tyrotoxicon*).—This poison consists of a special toxin which may be formed in cheese under certain circumstances.   It may be detected as follows : The cheese is triturated with water, filtered, rendered alkaline with soda and extracted with ether.   If the poison is present, the ethereal solution, on evaporation in a vacuum, deposits acicular crystals having an intense toxic action (to be ascertained by its physiological effect).

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In *judging a cheese*, the objective characters are first employed.   When struck on the rind, a *good cheese* should give a uniform sound ; the interior

48CHEESE

should be homogeneous and should not exhibit coloured spots; the taste should be normal and not bitter and the consistency normal and non-viscous. Further, a good cheese should contain no injurious or foreign substances and should have the quantity of fat considered normal.

According to the law passed in Italy in July, 1910, the tests to be made to ascertain if a cheese is pure are:

1. Separation of the fatty matter contained in the cheese.

2. Determination of the volatile fatty acids in such fat (Reichert-Meissl, Wollny number).

3. Determination of the index of refraction at 35° (with the Zeiss butyro-refractometer).

4. Determination of the percentage of fatty matter in the dry cheese. From the results obtained, the following deductions are drawn:

(1) If the *volatile acid number* is less than 18, the presence of margarine is denoted; if between 18 and 24, the cheese is suspect; if above 24, it is genuine.

(2) A higher *refractive index* than 48 proves the presence of margarine.

(3) The *percentage of fat* in the dry cheese serves as an orienting criterion, margarined cheese being usually poorer in fat than genuine cheese.

The *chemical composition of cheese* is variable and depends on the quality of the prime materials, the degree of ripening, etc.

CHAPTER III

FLOUR, STARCH AND DERIVED PRODUCTS

In this chapter are considered flour and starch and the products derived from them—bread, dextrin, macaroni and the like.

FLOUR

Flours are obtained by grinding cereals and seeds of certain leguminous and other plants. The most important are those of wheat, maize, rye and oats; of limited use are those of peas, beans and chestnuts.

Flour is usually analysed to ascertain if it is genuine and well stored, particularly from the hygienic standpoint, and to determine its commercial value as regards bread making.

The cases presenting themselves are usually as follows:

(*a*) To establish the nature of a flour. In this case microscopic examination (*see* 4, below) will indicate the origin of the flour and if it consists of one or several species.

(*b*) To determine if the flour is sound or unsound, altered or adulterated. In this case recourse is had to the external characters, the microscopic examination, the determination of water, ash, gluten, and acidity (5, 6, 7 and 8) and to tests for alteration, and for extraneous and harmful seeds, wood meal, foreign mineral substances and bleaching (*see* 9, 10, 11, 12, 13).

(*c*) To determine whether the material is fine flour, low products or mixtures. In such case use is made of the external characters, of the sieving test, of the microscopic examination and of determinations of the ash, gluten, acidity and cellulose (*see* 1, 2, 3, 4, 6, 7, 8, 15).

(*d*) To ascertain if a sound, unadulterated flour is more or less suited for bread-making: The ash and gluten are determined and practical baking tests carried out (*see* 6, 7, 14).

Complete analysis requires, besides the determinations indicated under (*b*), (*c*) and (*d*), also those of the carbohydrates, nitrogen (nitrogenous or protein products), fatty substances and, may be, phosphoric acid (*see* 16, 17, 18, 19).

Besides flour properly so-called, there are on the market prepared flours for special cooking purposes, for feeding infants, and for medicinal use, such as self-raising flour, oatmeal, gluten flour, milk flour, etc. In examining these products use is made of microscopic observation to ascertain the nature of the flour, and of the detection and determination of the sugars, saccharin, aromatic or colouring matters. Oat-meal, barley-meal, and the

like for dietetic foods are more or less torrefied and the torrefaction may be detected, besides by the odour and taste, also by determining the sugars and dextrin, which are in greater quantity in torrefied than in natural flour (*see* 16). With gluten flour, importance attaches to the determination of nitrogen (*see* 17), which indicates if gluten has been added.

Sampling.—When the sample is in sacks, portions are taken from the inner and outer parts and thoroughly mixed, and a similar procedure is followed with flour in cases or heaps. Of the mixture, the amount necessary for the analysis (about 500 grams) is stored, preferably in a glass bottle.

1. Objective Examination.—The flour is rubbed between the finger and thumb to ascertain if it is soft, lumpy, etc. ; it is also examined as regards odour (best observed in flours which are nearly unsound by boiling with water containing a little caustic soda) and taste (if agreeable or not) and for the presence of mites or other parasites visible to the naked eye or under a lens.

2. Colour.—This is determined by comparison with typical flours of known quality and of slightly differing colours :

On a shiny black wooden tray, 14 × 7 cm., provided with a handle, a parallelepipedon 5 × 3 cm. and 3 mm. deep is made with 15–20 grams of flour of known quality ; it is made smooth by compressing slightly with a glass plate and the edges cut sharp with a knife. Close to this a similar parallelepipedon is made of the flour to be examined. The tray, held obliquely, is then carefully lowered into a dish containing water (best acidified with sulphuric acid) and after about a minute slowly withdrawn and the colours of the two samples compared. Moulds may be used to facilitate the formation of the parallelepipons. Granular flour must be powdered before examination.

Such a test is of great importance in judging of the quality or fineness of flours. It is commonly made use of both commercially and to control milling.

3. Sieving Test.—This is usually carried out with a sieve of silk about 20 cm. in diameter and with 46 meshes per cm. 50 grams of the product to be examined are placed on the sieve, which is moved backwards and forwards by means of two wooden handles fitted at opposite sides inside a rectangular wooden framework ; the sieving should not last more than 10 minutes. The residue on the sieve is weighed and calculated as a percentage and the fine flour determined by difference.

The two portions thus separated are examined apart, both for their external and for their physical and chemical characters (especially ash-content, *see* 6).

This test is particularly important with inferior flour and fine bran.

4. Microscopic Examination.—This is an important test, as only by its help can the nature of a flour and its purity or mixture with other flour or extraneous substances be ascertained.

In practice, the test is based almost exclusively on the recognition of the starch granules, which exhibit characteristic shapes for starches derived from different plants.

It may be useful first to indicate certain practical points to be observed in using the microscope.

(*a*) PRACTICAL HINTS ON MICROSCOPY. A sufficient and uniform illumination of the field of vision is the first essential, use being made of diffused light of moderate intensity adjustable by means of an aperture in the diaphragm. Excessive illumination may cause the disappearance or render difficult the observance of fine structural details, especially with highly transparent preparations. When the field is properly illuminated and the preparation placed on the microscope, focussing is effected as follows : By means of the milled screw the microscope tube is lowered—being watched from the side and *not through the eye-piece*—until the objective is sufficiently near to the preparation ; this distance diminishes as the power of the objective increases. The observer then looks through the eye-piece and raises the tube slowly until focussing is exact. In this way the danger of forcing the front lens of the objective through the cover-slip is avoided.

The preparation is then passed under the objective, being kept in focus by means of slight, continuous movements of the micrometer screw ; this movement is very useful, especially with high magnifications, as it permits the images in different planes to be observed.

The magnification to be employed depends on the nature of the observation and on the object : for ordinary tests on flour, a maximum of 200–300 diameters is sufficient. In general it is convenient to make an examination first under a low magnification to obtain a general idea of the substance and to determine the interesting points in the preparation, the details being then studied under a higher power. In order to obtain a given magnification, it is best to use a high-power objective with a weak eye-piece, since the magnification of the image of the object is essentially the concern of the objective and on this consequently depends mostly the accuracy and sharpness of the image, whilst the eye-piece serves only to collect and magnify that image.

The microscope is kept away from dust, from sources of heat, and from the vapours of chemical reagents which would soon corrode the metallic parts and cloud the lenses.

(*b*) PROCEDURE. Several pinches of the flour from different points of a well-mixed homogeneous sample are mixed with water in a mortar until a milky liquid quite free from lumps is obtained. This liquid, kept in continuous motion, is poured on to a wide-meshed cloth stretched over the mouth of a beaker, in which the liquid containing the suspended starch is collected.

This liquid is well mixed and a drop removed on a glass rod to a microscope slide, covered with a cover-glass and observed under 200–300 diameters.

The starches are differentiated by the size and form of the granules, by the presence or absence of stratification and of a hilum, and lastly by the isolation or grouping together of the granules.

The microscopic characters of the commoner starch granules are described below and are seen distinctly in the figures (200 diameters) of Plates I–V.[1] In practice it is, however, useful to make a direct examina-

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[1] The micro-photographs were taken by G. Bosco,

tion of genuine samples of flour and to compare these with the flours under test.

This procedure is necessary in order to determine approximately the proportions in which different flours occur in a mixture. Under a low magnification, the number of granules of one of the starches of the mixture is counted in a number of fields. Comparison mixtures are then made and examined in the same way.

Besides examining the starch granules it is sometimes necessary, e.g. in mixtures of wheat and rye flours, and more particularly when it is desired to ascertain if a rye flour contains also wheat flour—where the granules do not differ sufficiently to allow of their certain detection—to make use of certain other elements present, namely, fragments of cortical tissue (bran) and hairs, the structure of which varies in different cereals.

Such elements are readily obtained from low grade flour, which is sieved and the residue washed to free it completely from the small amount of adherent flour. Before observing this residue under the microscope, it is well to heat it to incipient boiling with a 10% solution of sodium carbonate, which dissolves the cell-contents of the tissues and renders more distinct the structure of the walls.

With fine flour, the bran, fragments of hair, etc., are obtained as follows :

(a) 5 grams of the flour are boiled for 10 minutes in 100–150 c.c. of 10% hydrochloric or sulphuric acid containing 10 grams of glycerine. After settling, the liquid is decanted off, and the residue washed into a beaker with water, collected and examined.

(b) The separation may be effected mechanically by means of a liquid of density less than that of the starch granules and greater than that of the cortical residues. Such a liquid is a mixture of 75 parts of carbon tetrachloride and 25 parts of toluene.[1] With this liquid the flour is shaken in a cylindrical separating funnel and then allowed to settle. In a few minutes the bran floats in a brownish-yellow layer, while the flour is deposited at the bottom of the vessel. When the liquid is clear or but slightly opalescent, the tap is opened and the deposit formed allowed to escape. The shaking, deposition, etc., are repeated and the floating layer with the few c.c. of remaining liquid run on to a filter. The adherent particles are washed from the walls of the separating funnel with ether and the residues on the filter then completely washed.

This examination of the fragments of hair and bran is made more particularly to ascertain if a particular flour is a mixture of rye and wheat. The preparation is best compared, not merely with good figures and with the characters described in the text, but also with preparations made directly from grains of wheat and rye. As regards the hairs, it is easy with a good razor to detach a certain amount from the extremity of the seed where the hairs are collected in a tuft visible to the naked eye. To investigate the cortical tissue, the seeds are soaked for about a couple of hours in water, which is then heated to incipient boiling. By means of forceps with fine points it is easy to separate from the swollen seeds, when cold,

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[1] G. Testoni: *Le Staz. sper. agr. italiane*, 1915, XLVIII, p. 144.

fragments of epidermis which may be directly observed under the microscope.

The distinctive characters of the hairs and cortical tissues of wheat and rye are as follows :

Wheat hairs (*see* Plate I, Fig. 9). The walls of the hairs are of considerable thickness and even a little above the base exceed the width of the lumen. This lumen, which hence appears as a slender canal traversing the hair, widens sharply in the base sometimes with irregular notchings.

Rye hairs (*see* Plate I, Fig. 10). The walls are less thick than the lumen, which widens continuously from the apex of the hair to the base, where it forms a swelling parallel to the rounded outline of the base of the hair.

Cortical tissue of wheat. This consists of two layers of cells, the upper one lying transversely to the lower one. The length of the cells of the two layers is about the same, and their longer walls often exhibit very characteristic pearl- or disc-like swellings.

The shorter walls of the cells of the lower transverse layer are thinner than the longer walls and are joined so as to form a single wall separating two contiguous cells.

Cortical tissue of rye. The cells composing the two layers of the tissues corresponding with those studied for wheat are of different magnitude, those of the lower layer being markedly shorter than those of the upper, whilst the greater thickness of the longer walls, seen in wheat, is not observed in this case. Finally, the shorter walls of the cells of the lower transverse layer do not fuse with those of the contiguous cells, but remain independent, with small spaces between their points of contact.

(*c*) DESCRIPTION OF THE COMMONER STARCHES. These may be divided into starches from the endosperms of cereals, those from the seeds of leguminous plants and those from the tubers, rhizomes, medulla, fruits, etc., of other plants.

1. *Cereal starches.* The most important are the following :

Wheat starch (Plate I, Fig. 11). This forms isolated, circular granules varying in size, some having diameters of 20–40 μ and others on the average 6 μ ; they are mostly of globular form with polygonal surface. Few of the granules are intermediate in size between the large and small and no hilum or striation is observable.

Rye starch (Plate I, Fig. 12). Very similar to wheat starch, but of larger dimensions on the whole, granules of 60 μ being found and many of 40–50 μ ; granules with a point-like or, more often, stellate hilum with three or five rays are frequent.

Barley starch (Plate I, Fig. 13). This forms granules of the same type as the preceding, but smaller (maximum diameter, 30 μ), very small granules predominating. Their contour is less regular than that of wheat starch granules, and in some of them, especially the larger ones, is a kind of depression giving them somewhat the form of a kidney or bean.

Maize starch (Plate I, Fig. 14). These granules differ in form according as they are derived from the interior or the cortical part of the seed. The latter are characteristic in form and are almost all isolated, distinctly polyhedral, isodiametric and sensibly of the same magnitude (15–22 μ) ; they

have a central, often stellate hilum, but no stratification. The inner granules are also isolated, with a rounded edge, and have a hilum, but no stratification. This starch is easily distinguished from that of wheat, even in mixtures (Plate II, Fig. 15).

Buckwheat (Plate II, Fig. 16). This forms polyhedral granules, which measure 6–15 μ (mean, 10 μ) and have a hilum in the shape of a small central spot. These are sometimes united in large, characteristic groups, which are also polygonal and never rounded like those of rice and rye, from which they are hence easily distinguished.

Dhurra starch (Plate II, Fig. 17). This consists of granules very similar to those of maize starch, but less regular and uniform. As a rule, those of medium size—13–18 μ—predominate, but they are always mixed with much larger granules, 33–41 μ; many granules, instead of a stellate or linear hilum, present a characteristic structure radiating from the centre to the periphery.

Rice starch (Plate II, Fig. 18). This is highly characteristic and contains simple and compound granules. The former are polyhedral with 3–6 angles (most often, 5), are isodiametric and have a crystalline appearance; the mean dimensions are 4–6 μ. The compound granules, which are composed of simple granules, are rounded and have a spherical aspect with reticulated surface. These compound granules readily disaggregate into simple granules, especially during the mechanical operations directed to the separation of the starch, as in the preparation of face powder.

Oat starch (Plate II, Fig. 19). This consists of simple and compound granules. The former are small, polyhedral, and more irregular than rice starch granules, and also somewhat larger than the latter, the mean diameter being 7–9 μ. A characteristic, distinguishing this starch especially from rice starch—which never contains them—is the presence of a number of spindle-shaped granules, 12–18 μ long. The compound granules have a fairly regular oval contour and may attain a diameter of 60 μ.

2. *Leguminous starches.* The leguminous starches have characteristic and more or less similar aspects, which distinguish them from starches of other origins. They all have isolated granules of considerable size, the prevailing shape being oval, and they have a well-defined, more or less fringed, linear hilum and usually evident striation.

French bean starch (Plate II, Fig. 20). The granules have the form typical of leguminous starches. They are elliptical or bean- or kidney-shaped and all show a hilum fantastically fringed; the narrow striation is always plainly apparent. Mean length of granules, about 60 μ.

Broad bean starch (Plate III, Fig. 21). Granules similar to those of French bean starch, but less regular in outline. A hilum is rare and is linear and fringed. Narrow striation is usually apparent. Some granules reach the length 75 μ, but the mean length is 40 μ.

Chick peas starch (Plate III, Fig. 22). The granules of this starch are rounded oval in form and are among the smallest of the leguminous starches, the maximum length being about 28–30 μ. A hilum is not frequent, whilst striation is fairly evident.

Pea starch (Plate III, Fig. 23). The granules of this starch are more

rounded in contour than those of the other leguminous starches and some-
times exhibit a conical form. The cavity-like hilum and the striation are
visible only in certain granules. The mean dimensions are about 45 μ.

Lentil starch (Plate III, Fig. 24). These granules resemble in contour
those of pea starch, but the hilum is more frequently seen and represents
an irregular cavity; striation is almost always observed. The mean
diameter of the granules is 38–40 μ.

Vetch starch (Plate III, Fig. 25). This consists of rounded oval, some-
times hunch-backed granules, exhibiting an irregular, fringed hilum and
sometimes indistinct striation. The medium granules are 30 μ in diameter,
but the smallest are only 7–10 μ.

3. *Starches of tubers, roots, stems, etc.* The more important of these are:

Potato starch (Plate III, Fig. 26). Isolated granules of variable magni-
tude, the diameter reaching as much as 100 μ, though the mean value is
45–65 μ. The small granules are mostly oval and the larger ones are ovoid,
but more irregular, and sometimes wedge-, rhomb- or shell-shaped. All the
granules exhibit distinct striation and an eccentric point-like hilum. Some-
times special, semi-composite granules are found, with a double striation
orientated round two or three centres.

Sweet potato starch (Plate IV, Fig. 27). This consists of granules of
irregular form and size. The typical shape is rounded with four angles,
somewhat like an egg or a kettle, and some granules are striated and exhibit
a well-marked eccentric hilum. The mean size is 30 μ, but the largest
granules may attain 65 μ.

Maranta (arrowroot) starch (Plate IV, Fig. 28). The granules in this
case are rounded and pear-shaped or, more rarely, trapezoidal. Their
mean diameter is 30–40 μ, the limits being 50 μ and 12 μ; as the medium
granules predominate, the starch has a uniform appearance under the
microscope. All the granules are finely striated round a hilum which
occupies either the centre or, more often, a point nearer one end; the
hilum is highly characteristic and consists of two short rays meeting at a
wide angle like a circumflex accent or, better, the open wings of a bird.
Some few granules show a small cavity instead of such hilum.

Sago starch (Plate IV, Fig. 29). This consists of simple and compound
granules. The former are very large (50–65 μ), oval or elliptical and strati-
fied, and they contain a hilum which may be point-like or linear or in the
form of a radiating cavity. Before being imported to Europe this starch
is, however, treated (heated) more or less, so that the granules are altered
in appearance, especially as regards the hilum, which tends to change to
a cavity with radial fissures. The compound granules consist of a large
granule to which are united two or more small granules of the mean diameter
15 μ. These compound granules have, therefore, a hunch-back appearance,
and if the smaller granules become detached, the surface left appears flat.
Such flat parts of the contour of the granule are distinctive characters very
useful for identifying this starch.

Manioc starch (Plate IV, Fig 30). The granules are globular and often
resemble a kettle or drum, exhibiting a round and also a flat part. The
large granules may attain a diameter of 36 μ, the medium ones are 18–22 μ,

while the small ones are sometimes only 5 μ. Most of the granules contain a readily visible hilum in the form of a small cavity. Further, compound granules, composed of two or, rarely, three granules of different sizes, are often observed.

East Indian arrowroot starch (Curcuma angustifolia) (Plate IV, Fig. 31). The granules are isolated and characterised by one rounded and one pointed extremity, the appearance being that of a lance-head. Some granules, when viewed from the side, resemble a very elongated spindle. All contain an eccentric hilum and show fine striation. The mean length is 40–60 μ and the mean breadth 30–35 μ.

Chestnut starch (Plate IV, Fig. 32). The granules are mostly isolated, with a rounded contour and a diameter of 15–20 μ. The typical forms are pear- and bottle-shaped with a slightly undulating outline. Hilum and striation are usually absent.

5. Determination of Water.—10 grams of the flour, dried in a platinum dish for 5–6 hours in an air-oven at 105–110°, are cooled in a desiccator and quickly weighed: loss equals moisture.

This determination is of importance especially as regards the keeping quali-ties, and is also necessary when the analytical data are to be referred to the dry flour for purposes of comparison with other flours. The moisture varies in amount somewhat with the hygrometric state of the air and may be 1–2% more in winter or wet weather than in summer.

6. Ash.—10 grams of the flour (that from the preceding test may be used, if it does not fill the dish to more than two-thirds) are heated gradually over a naked flame until charred, the dish being then placed in a muffle at a dull red heat until the carbon is completely burnt. The temperature of the muffle should not be too high, since otherwise the ash fuses and the carbon does not burn completely.

The ash from low products (offal, bran) is usually dark; in such a case it is well to treat the ash in the dish with a little distilled water, to dry the whole on a water-bath and then over a naked flame and again place in the muffle.

The ash may be treated with hydrochloric acid to ascertain if it is almost all soluble or if it contains sand.

This determination is of importance in judging of the grade of a flour, since the proportion of ash increases in passing from superior to inferior flours.

7. Gluten.—This may be determined in either the wet or the dry state.

(a) WET STATE. 25 grams of the flour are made into a homogene-ous paste with 12–12·5 c.c. of tap water in a porcelain mortar and left for half an hour. The paste is then worked carefully between the hands under a gentle stream of water at 15–20°, the water being passed subse-quently through a fine sieve. The gluten is gradually agglomerated into a soft, elastic mass, while the starch is carried away by the water; when the latter flows away fairly clear the stream is increased, and when this also becomes clear the operation, which requires about 15 minutes, is at an end. The gluten thus obtained, together with any small particles which may have fallen on to the sieve, is freed from excess of water by squeezing

in each hand alternately, the hand being dried meanwhile on a towel ; when no more moisture is given up to the hand, the gluten is weighed on a clockglass.

The external characters (colour, odour, elasticity and tenacity) of the gluten indicate its quality and so the behaviour of the flour as regards bread-making.

Special apparatus may be used by means of which the swelling power of the gluten on heating is determined, but the indications thus obtained are in no way more valuable than those of a qualitative study of the external characters.

(b) Dry State. The dry gluten may be calculated approximately from the percentage of moist gluten by dividing by three. A more exact direct determination may be made as follows :

The gluten obtained as in (a) is dried on a nickel plate in an air-oven at 105° to constant weight, this requiring about 20 hours. A more rapid procedure consists in flattening the gluten out on the nickel plate by means of the finger and drying at 120° for 2·5–3·5 hours. The weight is referred to 100 parts of flour.[1]

With practice this method gives concordant results. As regards the extraction of the gluten, this is easy with fine wheat flour and ordinary bread flour, but difficult with inferior flours, and the latter may conveniently be manipulated under the water in a thin linen bag. Flours of other cereals do not yield gluten when treated in this way.

8. Acidity.—5 grams of the flour and 25 c.c. of 90% alcohol, neutralised exactly with N/20-caustic soda solution, are shaken at intervals during a day in a cylinder with a ground stopper. After standing overnight, 10 c.c. of the clear liquid are titrated with N/20-caustic soda in presence of phenolphthalein or tincture of turmeric.[2]

The acidity is expressed as either sulphuric or lactic acid : 1 c.c. N/20-soda = 0·00245 gram H_2SO_4 or 0·0045 gram $C_3H_6O_3$. It may also be expressed simply as the number of c.c. of normal soda required per 100 grams of flour, this being termed the *degree of acidity*.

The acidity, ash, external characters, colour and gluten furnish the best data for valuing flour.

Besides by the above method, the acidity is determined also by other methods, sometimes alcohol and sometimes water being used as solvent ; the alcohol methods are to be preferred. Results are comparable only when obtained by the same method, which should always be indicated.

9. Detection of Alterations.—When badly stored, especially in moist surroundings, wheat flour undergoes change with development of a disagreeable odour and sharp taste in consequence of attack by various moulds. Certain changes arise from diseases of the grain such as smut (Ustilago carbo), rust (Uredo linearis), bunt (Tilletia caries), etc. The presence of the moulds or spores is detected to some extent by the physical examination and is rendered certain by microscopical examination.

[1] Neumann and Salecker : *Zeitschr. Unt. Nahr- u. Genuss-mittel*, 1908, I, p. 735.
[2] Tincture of turmeric is prepared by macerating 1 part of powdered turmeric root with 10 parts of 60% alcohol for some days and filtering the alcoholic extract. It is best to follow the procedure indicated in the chapter on flesh foods (p. 8, note).

Other changes are due to the presence of mites and of the larvæ of insects, especially those of the yellow meal-worm (Tenebrio molitor) and the Mediterranean flour-moth (Ephestia Kühniella). Larvæ of insects are detectable by the naked eye. Mites may easily be observed by pressing a spoonful of flour on a sheet of paper with a transparent sheet of glass : any mites present soon begin to move and render the surface of the flour in contact with the glass streaked with numerous irregular furrows.

Maize flour undergoes change still more readily and hence cannot be kept long. The changes occurring, which may even lead to illness owing to the formation of toxic principles, are due to numerous causes, but more particularly to excess of moisture. They are detected mainly by the objective characters and by microscopic examination. Further, they may be recognised by various reactions, such as the phenol, hydrogen peroxide and coumarin reactions, but long practice with these is necessary to base on them a sound judgment as to the state of conservation of maize and its derivatives.[1]

10. Detection of the Products of Extraneous and Injurious Seeds. —Extraneous seeds, the flour or fragments of which occur in wheaten and other flours, owe their presence mainly to careless harvesting of the grain. These seeds are principally : vetch (Vicia sativa, alba, Ervum ervilia, etc.), bindweed (Convolvulus arvensis, Polygonum convolvulus), darnel (Lolium temulentum), corn-cockle (Agrostemma githago), narrow-leaved everlasting pea or wood vetchling (Lathyrus silvestris), meadow vetchling (Lathyrus pratensis), everlasting pea (Lathyrus aphaca), and cow wheat (Melampyrum arvensis). The darnel, corn-cockle, melampyrum and Lathyrus aphaca are poisonous ; also the ergot (Claviceps purpurea), which is poisonous, may sometimes be found in flour.

The above impurities may be detected by microscopical comparison of the flour with preparations of the seeds mentioned, and are also rendered evident by the following tests :

(a) A small quantity (5–10 grams) of the flour is spread in a thin, uniform layer on a smooth white plate and sprinkled as evenly as possible with Vogl's mixture (100 parts of 70% alcohol and 5 parts of hydrochloric acid). The plate is then heated over a flame until steam begins to appear and the flour examined for small discoloured areas or blackish spots.

The latter indicate corn-cockle, vetch, ergot or mites ; coloured spots— usually red, violet or blue—justify suspicion of the presence of darnel, lathyrus, melampyrum, or other seeds the perisperms of which contain special pigments reacting with Vogl's acid solution.

These different elements are collected on the point of a needle for microscopic examination, under first a low, and then, if necessary, a high magnification.

(b) 20 grams of the defatted flour are heated with 80 grams of chloroform and 20 of absolute alcohol and filtered hot by means of a pump. The filtrate is evaporated on a water-bath and the residue taken up in a little hot water, filtered and again evaporated. If any considerable residue is left, the flour is suspected of containing corn-cockle, the presence of which

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[1] B. Gosio : *Alterazioni del granoturco e loro profilassi*, Rome, 1909.

is confirmed if the residue is turned yellow and then brownish-red by a few drops of concentrated sulphuric acid.[1]

(c) From 5 to 6 grams of the flour are made into a paste with 10% hydrochloric acid and the paste spread out on glass, heated until the acid evaporates, and examined for coloured spots. In presence of *melampyrum* greenish points or spots appear, while darnel or Lathyrus aphaca gives a red coloration. If *darnel* alone is present the coloration is shown immediately and in the cold and is red, tending to orange; with Lathyrus aphaca the colour appears best in the hot and is wine-red. To distinguish between these two the red fragments are examined.[2]

(d) From 10 to 15 grams of the flour are treated with 20–30 c.c. of ether and 10 drops of dilute sulphuric acid (1 : 5) and shaken from time to time during 5–6 hours; the mass is then filtered and washed with 20–30 c.c. of ether and the ethereal liquid treated with 10–15 drops of cold, saturated sodium bicarbonate solution. A violet coloration indicates *ergot* (Hofmann and Hilger's reaction).

(e) The flour is treated with water rendered alkaline; violet spots will appear if *ergot* is present.

(f) In presence of *ergot*, a disagreeable odour of trimethylamine is emitted when the flour is heated with 10% potassium hydroxide solution.

The last reaction is also given by flour altered by decomposition.

11. Wood-meal.—To inferior flours and especially to low semolinas for fodder, bran, and the like, additions are sometimes made of wood-meal, arachis husk, ivory-nut meal, etc.

To detect *wood-meal* the flour is spread out on a flat-bottomed porcelain dish, compressed and then gently heated with 0.1% alcoholic phloroglucinol solution acidified with 50% sulphuric acid and examined for carmine-red spots. Any woody particles are coloured immediately, whilst the critical residues of the wheat become coloured only after some time.

Ivory-nut meal [Plate V (at end of chapter), Fig. 38] is detected by the following microscopical test: The flour is treated with 3% soda solution and left for half an hour, after which the liquid is decanted off and the residue washed with water and examined under the microscope. The ivory-nut meal is readily recognised by its characteristic structure, since the cells of the endosperm of this seed exhibit an enormous thickening of the walls, so that the aperture of the cell is distinctly reduced. These thickenings are interrupted here and there by channels connecting the cells.[3]

Another test for the detection of ivory-nut meal is as follows[4]: 5 grams of the flour are shaken in a separating funnel with chloroform and left at rest for 6 hours. Any ivory-nut meal present is then deposited on the bottom of the funnel and is examined microscopically, any extraneous mineral matter being removed by the treatment given above.

12. Extraneous Mineral Matter.—Flour may contain sand or earth

[1] Medicus and Kober : *Zeitschr. Nahr- und Genuss-mittel*, 1902, V, p. 107.
[2] G. D'Ippolito : *Staz. sper. agrar. italiane*, 1910, p. 585.
[3] E. Bertarelli : *Accad. reale di medicina in Torino*, Nov. 23, 1906.
[4] J. Gerum : *Zeitschr. Nahr- u. Genuss-mittel*, 1914, V, p. 392.

arising from imperfect cleaning, gypsum, calcium carbonate and other mineral salts (alum, zinc, copper and lead salts) added for various purposes or derived from the grinding machinery.

The presence of mineral substances is detected as follows :

(*a*) SAND, EARTH, GYPSUM, CALCIUM CARBONATE, ETC. 5 grams of flour are shaken in a test-tube with 25 c.c. of chloroform, a few drops of water being then added and the whole left. The flour floats, but the extraneous mineral matters are deposited at the bottom of the liquid and are characterised by collecting them with the help of a small separating funnel and analysing them systematically. Flour containing ivory-nut meal (*see* 11) also yields a sediment under this treatment.

(*b*) LEAD, COPPER, ETC. These are tested for in the ash obtained by burning about 200 grams of the flour.

(*c*) ALUM. 20 grams of the flour are ashed as described in 6 (above), the ash being boiled with water and filtered. A small portion of the aqueous solution is acidified with hydrochloric acid and treated with barium chloride : if alum is present, a white precipitate is formed. The presence of alum is confirmed by adding ammonium chloride and ammonia to the remainder of the aqueous solution : a white flocculent precipitate will be obtained. For further confirmation, the precipitate is collected on a small filter and dissolved in hydrochloric acid, the solution being treated with slight excess of potassium hydroxide and filtered and the filtrate treated with ammonium chloride : a white precipitate proves the presence of aluminium.

Among the mineral substances naturally contained in flour, aluminium is found either not at all or only in traces. The quantity of alum sometimes added to flour is 0·3%, corresponding with 0·03% of alumina.

(*d*) ZINC SALTS. In a suitable round-bottomed flask, 25 grams of the flour are shaken with 30 c.c. of conc. sulphuric acid and 5–10 grams of potassium sulphate until the mass chars, this usually requiring about 10 minutes in the cold. The flask is then heated over a small flame, conc. sulphuric acid being added in quantities of 10 c.c. every 10 minutes or so and later, after half an hour, 65 c.c. ; the whole is then strongly heated under a hood until the liquid becomes quite clear. The acid residue, if more than 20 c.c., is further concentrated in a platinum dish and then diluted with water to about 250 c.c., any ferrous sulphate present being oxidised by means of nitric acid in the hot. The cold liquid is treated with excess of ammonia and filtered, and the filtrate acidified with acetic acid and treated with hydrogen sulphide. If any white precipitate (zinc sulphide) forms, the liquid is diluted with water and the precipitate allowed to settle for 24 hours and then collected on a filter, washed successively with hydrogen sulphide solution and with water containing ammonium nitrate, ignited over a small flame and weighed as zinc oxide.

For detecting other metals than zinc it is convenient to destroy the organic matter as described above and to examine the diluted acid solution by the ordinary analytical methods.

13. Detection of Bleaching.—Flour is often artificially bleached to improve its aspect and increase its market value. This bleaching is usually

effected by means of air mixed with oxides of nitrogen (nitrogen peroxide, etc.) and is detected as follows :

Reagent. Sulphanilic acid (0·5 gram) and α-naphthylamine (0·1 gram) are each dissolved in 150 c.c. of 30% acetic acid and the solutions then mixed. The vessels in which the solutions are prepared should previously be washed with acetic acid. In some cases the mixture exhibits a faint red coloration, which is removed by addition of zinc dust ; also after long standing this coloration may appear, but it is prevented by the presence of zinc dust.

Procedure. From 3 to 5 drops of this reagent are placed on a quantity of the flour spread out and pressed flat, as in determining the colour (*see 2*, above) and any coloration noted. With bleached flour a pink or red colour appears after a few seconds or, in any case, before the lapse of a minute, whereas untreated flour is not coloured.[1]

14. Practical Baking Tests.—Those most generally employed are as follows :

(*a*) WATER-ABSORBING POWER. The absorbing power of 100 parts of flour towards water is determined and hence its behaviour as regards formation of dough. The determination is made as follows :

A definite quantity of the flour (about 100 grams) is placed in a porcelain dish and a small depression made on the surface by means of a convex object. 25 c.c. of water are added and the whole mixed with a glass rod to make a paste adherent to the rod. This dough is then placed on the palm of the hand sprinkled with the flour and more flour added and mixed until a dough is obtained which does not adhere to the finger. The dough is then weighed (*P*) and the water used calculated by means of the formula, $A = \dfrac{2500}{P - 25}$. Three measurements should be made and the mean of the results taken.

This test gives only relative values, and for a determination more in consonance with practice, a larger quantity of water—say 10 litres—is taken and doughed with the necessary amount of flour.

(*b*) BAKING TEST. This is best made on 10–15 kilos of flour by a person experienced in practical baking.

For laboratory tests use may be made of a small jacketed metal oven containing heavy mineral oil and coated with asbestos board ; it is heated by gas and serves to bake loaves of about 150–200 grams prepared by doughing 1 kilo of flour with the required amount of water (about 500 c.c.), 1% of sodium chloride and 20 grams of beer (or pressed) yeast being added and the whole left to rise for 2 hours in an oven at 30–33° C.

The loaves prepared on either the large or the small scale are examined as to their external appearance, and in section to ascertain their porosity, the thickness of the crust, the adherence of the latter to the crumb, etc., and also as to their objective characters. Further, since the value of a flour for bread-making increases with the volume of the loaf, the latter is often determined. To this end loaves are prepared as above from 100–200

[1] Buchwald and Neumann : *Zeitschr. f. das ges. Getreidewesen*, 1909, p. 135.

grams of flour, which is doughed with water, salt and yeast in quantities proportional to those already given and then allowed to rise and baked.

The *volume* is determined by the displacement of solid bodies, such as glass balls, lead shot or small seeds (rape, millet, etc.), in the following manner : A large funnel closed at the bottom is charged with one of these substances, preferably seeds, which are then run into a thick-walled, wide-necked cylinder until the latter is heaped over, the excess being struck off with a straight-edge ; the volume of this seed is then ascertained by pouring it through a funnel into a measuring cylinder. Part of the seed is then returned to the wide-necked cylinder, the loaf being introduced and afterwards more seed until the vessel is heaped over with them. After striking off the excess, the volume remaining with the loaf is measured. The volume in c.c. of the loaf yielded by 100 grams of the flour is calculated.

Laboratory baking tests are of only relative value, the safest criterion being found in tests made on the practical scale.

15. Determination of the Cellulose.—By cellulose or, more properly, crude cellulose, is meant that portion remaining undissolved when cereals or their ground products are treated with acid or alkali of definite concentration. Various methods of determining it have been proposed, two in general use being as follows :

I. MILLON'S METHOD. This includes three operations : (*a*) elimination of fat ; (*b*) treatment with hydrochloric acid (D 1·025) ; (*c*) treatment with dilute alkali (about 1%).

(*a*) *Elimination of fatty matter.* This may be effected in a Soxhlet extraction apparatus, but a more rapid method consists in placing a weighed quantity (20 grams for ordinary flour, 10 for inferior flour and 2·5–5 for bran) on a short-stemmed funnel in the bottom of which is a certain quantity of a soluble salt (dry sodium chloride) and in washing, first with a little alcohol and then with anhydrous ether, until this runs through colourless and leaves no residue on evaporation ; the funnel is then dried for a short time in a steam-oven to expel the ether and treated as follows :

(*b*) *Treatment with hydrochloric acid* (D 1·025). The funnel with the substance and salt is placed on a flask holding about 600 c.c., the mass being pierced with a glass rod and pushed down into the flask, the funnel and the neck of the flask being then washed with hydrochloric acid (D 1·025), 400 c.c. in all being used. The liquid is then carefully boiled under a reflux condenser for half an hour, care being taken to shake the liquid during the first phase of the heating so as to prevent the collection of lumps on the bottom of the flask and consequent charring. The hot liquid is filtered through a rapid (hardened) filter, finally with gentle aspiration by means of a pump, the flask and the residue on the filter being washed first with hot acid (D 1·025) and then with a little hot water.

(*c*) *Treatment with potash.* The residue is detached from the filter (without breaking this) by means of a jet of hot water and collected, with the help of a funnel, in the flask previously used ; it is then boiled for half an hour with 50 c.c. of 5% potassium hydroxide solution and enough water to bring the volume up to 300 c.c., and filtered hot through a tared Gooch

crucible containing a shallow layer of asbestos, a perforated porcelain disc, and a second layer of asbestos. The filtration is rapid at first, but usually slackens gradually ; in this case, when all the liquid in the crucible has passed through, the residue is gently moved with a jet of water and the filtration continued. The residue is washed with hot water until the filtrate ceases to show an alkaline reaction, then with a little alcohol and finally with a little ether ; the crucible is dried for two hours at 105° and weighed. The crucible is then ignited and its weight, with the small amount of mineral matter from the fibre, determined. The difference between the two weights represents crude cellulose free from mineral matter.

2. KÖNIG'S METHOD. 5 grams of the substance are boiled for an hour in a reflux apparatus with 200 c.c. of about 85% glycerine (specific gravity 1·23) containing 2% of concentrated sulphuric acid. The liquid is cooled, mixed with 200 c.c. of distilled water, heated to boiling and the hot liquid filtered through a Gooch or alundum filter with the help of a pump. The residue is washed with about 400 c.c. of boiling water, then with alcohol, and finally with a mixture of alcohol and ether until the liquid passes through colourless ; it is then dried at 105° for an hour and weighed. To allow for the mineral substances present in the cellulose, the procedure followed in the previous method is employed.

16. Determination of the Carbohydrates (Starch, Sugar, Dextrin, Pentosans).—Of the carbohydrates contained in flour, namely, starch, sugars, dextrin and pentosans, the starch is in the greatest proportion. These constituents are usually estimated by difference after the water, mineral salts, nitrogenous substances, fats and cellulose have been determined, and they are usually comprised under the generic name *non-nitrogenous extractives*. If a direct determination is desired, the following methods may be employed :

1. SUGARS. From 5 to 10 grams of the flour are shaken in a litre flask with distilled water ; after standing, the liquid is syphoned off and the reducing sugars in an aliquot part of it, concentrated if necessary, determined with Fehling's solution (*see* chapter : Sugars).

2. DEXTRIN. Part of the liquid used for the preceding determination is hydrolysed with hydrochloric acid of D = 1·125 (which transforms the dextrin into dextrose) and then neutralised, the sugars being determined as before. The difference between the result and that of determination 1 gives the sugar due to the dextrin and multiplication by 0·9 gives the dextrin.

In general sugars and dextrin are not determined in practice unless it is desired to know exactly the percentage composition of a flour or to ascertain the starch by difference. The determination of the dextrin may be useful in deciding if a flour has been torrefied or not.

3. STARCH. This may be determined by the two following methods :

(a) *By inversion.* 2 grams of the flour are placed in a Lintner-Rempel pressure bottle with 40 c.c. of water and heated for 3 hours at 130–140° in a paraffin bath. When cold, the contents of the bottle are washed out with several quantities of 40 c.c. of water into a flask (about 250 c.c.), the liquid being treated with 10–15 c.c. of hydrochloric acid (D 1·10–1·12) and boiled for half an hour under a reflux condenser. In this way the

starch is converted into glucose. After rapid cooling, the liquid is neutralised with 10% potassium hydroxide solution, treated with a few drops of lead acetate to clarify it more readily, transferred into a 200 c.c. measuring flask and made up to volume with the wash waters of the first vessel. After standing for a short time, the liquid is filtered and the sugar determined in the filtrate by means of Fehling's solution—with the ordinary precautions (see chapter : Sugars)—and calculated as dextrose.

From the dextrose found that found in the determination of the dextrin is subtracted and the remainder, multiplied by 0·9, gives the starch in the flour.

Since sugar and dextrin occur in flour in only small proportions, some authors neglect them and calculate the starch simply by multiplying the total dextrose found by 0·9.

(b) *Polarimetrically*. According to Lintner,[1] the following procedure is employed :

Of the finely divided product, 2·5 grams are mixed to a paste with 10 c.c. of water in a dish, 15–20 c.c. of hydrochloric acid (D 1·19) being added with stirring to obtain a homogeneous mass. After half an hour's rest, the whole is transferred, with addition of hydrochloric acid (D 1·125), into a 100 c.c. flask, defecated with 5 c.c. of 4% phosphotungstic acid solution and filtered, the polarisation of the filtrate being determined in a 20 cm. tube in a yellow light instrument.

Since the specific rotation of starch saccharified under these conditions has been found by experiment to be $[a]_\mathrm{D} = + 202°$, the percentage of starch, a, in the flour is given by $a = 9·9\ P$, P being the rotation observed.

If a Soleil-Ventzke saccharimeter is used (a Mohr flask being used to make up the liquid to 100 c.c.), a will be given by $3·43\ R$, where R is the number of scale divisions when a 20 cm. tube is used.

In the polarimetric determination of starch, sulphuric acid may be used for the saccharification as described by Miller.[2]

In most cases the determination of starch is not of great importance in the analysis of flour. Besides in the complete analysis of flour, it may be useful in the analysis of brans, in order to indicate if the whole or only part of the flour has been removed.

4. PENTOSANS. This determination is made by Tollens and Krüger's method, which is based on the transformation of pentosans into furfural by distillation with hydrochloric acid and on subsequent precipitation of the furfural with phloroglucinol. The analysis comprises, therefore, two distinct operations :

(a) *Formation and distillation of the furfural*. The weighed substance (5 grams with flour, 3 with middlings and 1 with bran) and 100 c.c. of hydrochloric acid (D = 1·06) is placed in a flask of about 300 c.c. capacity, fitted with a tapped funnel and connected with a condenser. The flask is immersed in an oil-bath at 150° C. and 30 c.c. of distillate collected ; without interruption of the distillation, a further 30 c.c. of the acid is added and another

[1] *Zeitschr. Unt. Nahr- u. Genuss-mittel*, 1907, XIV, p. 205.

[2] *Zeitschr. f. das ges. Getreidewesen*, 1909, p. 217 ; and *Ann. Lalor. Chim. Cent. Gabelle*, Vol. VII. p. 111.

30 c.c. of distillate collected. This procedure is continued until all the furfural is expelled and a drop of the distillate fails to give a red coloration with a drop of aniline acetate (9 parts of colourless aniline + 6 parts of acetic acid) on filter-paper.

(b) *Precipitation of the phloroglucide.* The distillate is treated with phloroglucinol (puriss.) dissolved in hydrochloric acid (D 1·06) in amount about double that of the furfural supposed to be present, i.e. 0·2 gram for ordinary flour or 0·4 gram for middlings and bran ; the liquid is made up to 400 c.c. with the same hydrochloric acid, stirred with a glass rod and left at rest for 15–18 hours. After 3 hours, a drop of the liquid is treated on filter-paper with the aniline acetate solution ; if a red coloration is formed, a little more phloroglucinol is added to the liquid. The precipitate is ultimately collected on a filter previously dried at 100° C. and tared, washed with water (150 c.c. in all), dried between filter papers and then in a steam-oven for 3–4 hours, and weighed.

(c) *Calculation of the pentosans.* The weight of the furfural is determined by dividing that of the phloroglucide by the corresponding factor of the following table :

Weight of Phloroglucide.	Divisor for Calculation of the Furfural.	Weight of Phloroglucide.	Divisor for Calculation of the Furfural.
0·20	1·820	0·34	1·911
0·22	1·839	0·36	1·916
0·24	1·856	0·38	1·919
0·26	1·871	0·40	1·920
0·28	1·884	0·45	1·927
0·30	1·895	0·50	1·930
0·32	1·904	0·60	1·930

Then, (furfural $- 0.0104$) $\times 1.88 =$ pentosans.

A complete table giving, for different weights of phloroglucide, the corresponding weights of furfural and arabinose, araban, xylose, xylan, pentose and pentosan, has been compiled by Tollens and Krober.

With products from wheat-milling, it is sometimes necessary to distil more than 400 c.c. to obtain all the furfural ; in such case, the distillate collected after 400 c.c. have passed over is treated separately with a small quantity of phloroglucinol and the precipitate formed weighed separately.

17. Determination of the Nitrogen.—The Kjeldahl-Ulsch method is used, about 2 grams of the flour being treated with 20 c.c. of the phosphoric-sulphuric acid mixture (*see* Fertilisers, Vol. I, p. 122) : N $\times 6.25 =$ *nitrogenous substances* in general or *proteins.*

The proteins of flour are usually distinguished, according to their behaviour with 70% alcohol, as gliadin (soluble) and glutenin (insoluble).

Gliadin is determined directly by treating 10 grams of the flour with 100 c.c. of 70% alcohol in a glass cylinder with a ground stopper, with frequent shaking during the day. After standing overnight it is again shaken

in the morning and, when the flour has settled, filtered.   The total nitrogen is determined in 50 c.c. of the filtrate by evaporating almost completely with a little phosphoric-sulphuric acid, then adding the remainder of the acid and proceeding as usual : N × 6·25 = gliadin, which is then calculated on the total nitrogenous substances.   The *glutenin* is calculated by difference.

It is held by some that the relation between the amounts of gliadin and glutenin determines the baking quality of a flour, but this is not confirmed in all cases.

18. Fatty Substances.—5 grams of flour previously dehydrated at 105° are mixed with an equal amount of siliceous sand and treated in one or the other ordinary extraction apparatus with anhydrous ether or petroleum ether : the fat is calculated on either the dry or moist flour.

Results thus obtained are sufficiently exact for ordinary purposes, but more exact numbers are given by the procedure described for bread (*q.v.*).   In flour, the fatty substances and the ash run parallel.

19. Phosphoric Acid.—The ash obtained from 25 grams of flour, burnt in presence of 1 gram of a mixture of nitre (1 part) and sodium carbonate (3 parts), is treated as indicated for wine (*q.v.*), the result being expressed as phosphoric anhydride.

$$*_*^*$$

The characters of *wheaten flour for bread-making* are given below, the numbers referring to flour with the normal proportion of water (13%).
Physical characters.   The flour should be soft to the feel, of pleasing smell and taste, free from any trace of rancidity or mould, or of mites or other parasites.
Colour.   The best brands and those used for pastry are white with a slight yellow cast ; those for bread vary in whiteness, the lower qualities being dirty white or grey.
Sieving test.   No appreciable residue should be left on a sieve with 46 meshes per cm., except in the case of granular flours.
Microscopic examination.   Flour should not contain substances extraneous to wheat or injurious seeds (darnel, corn-cockle, melampyrum, ergot, etc.).
Water.   This varies from 10 to 15%, more generally from 12 to 14%.
Ash and mineral matter.   These vary according to the degree of fineness, i.e. according as the bran has been removed to a greater or less extent and, consequently, according to the process of milling adopted.   When a single type of flour, containing 70–80% of the wheat, is produced, the mean ash-content is 0·7–0·8% (0·8–0·92 on the dry matter), but when, as is usual, various types of flour (numbered differently according to the mills used) are made, the ash-content may increase from a minimum of 0·3% (0·34% on the dry matter) to 1% (1·15% on the dry matter).
The ash is almost completely soluble in hydrochloric acid ; the insoluble part, consisting of sand and earth, should not exceed 0·3% of the flour.   About 50% of the ash is phosphoric anhydride, the remainder being oxides of potassium, calcium, magnesium, sodium and iron, with traces of silica and chlorine.   Lead, copper, zinc and alum should be absent.
Gluten.   This is yellowish or pale grey, of pleasant odour, tenacious and elastic ; it should be stretchable in all directions without breaking and when ʳeleased should regain its original form.   These properties, which are related

to more or less good baking properties, are found especially in the glutens of flours with the lowest proportions of ash ; with increase of the latter, the gluten gradually becomes darker, less tenacious and less elastic. The quantity of dry gluten in flour usually varies from 8 to 12% (9–13·7% on the dry matter), according to the quality of the wheat and the season ; it may, however, sometimes exceed 12% (13·7% on the dry matter).

Acidity. This increases with the ash, and also varies with the season and state of preservation of the flour, the proportion of acid increasing with the age and with poor storage conditions. New flours have acidities lying between 0·04 and 0·08% (0·046–0·092 on the dry matter), expressed as sulphuric acid and determined by the method given above (*see* 8) ; in no case should the value exceed 0·10% (0·115% on the dry matter). In old or badly stored flour these limits are exceeded.

Practical tests relating to baking :

(a) *Water absorption.* This is, on the average, 60% for normal flours. Good flour gives an elastic dough, which may be pulled out and apparently keeps its shape even when left to itself for 24 hours. Altered flour yields a dough which readily breaks when pulled ; it becomes shiny on the surface after a short time and later turns viscous and loses its original form.

(b) *Baking test.* A good flour gives a loaf of volume not less than 400 c.c. per 100 grams of flour ; the bread should be porous and tasty, the crust pale and the crumb moderately brown. A flour giving a small loaf is never good.

Cellulose (method 15, above). In first quality flour, the cellulose does not exceed 0·3% (0·34% on the dry matter). It increases in the lower qualities up to 1% (1·15% on the dry matter) for flour with a high ash. Wood-meal, ivory-nut meal and the like should not be present.

Soluble carbohydrates (sugars, dextrin). These increase in amount with increase of the ash, the limits being 0·8–2·0% (0·9–2·3% on the dry matter).

Starch. This varies inversely with the ash, nitrogen, fats, cellulose and soluble carbohydrates, the limits being 60–72% (68–82% on the dry matter).

Pentosans. These increase with the ash and cellulose, the amount varying from 3 to 5% (3·4–5·7% on the dry matter).

Nitrogenous substances (N × 6·25). These are related to the percentage of dry gluten but usually exceed 0·5–1·0%, calculated on the flour.

Fat. This varies in the same direction as the ash, the amount usually lying between 0·5 and 1% (0·57–1·15% on the dry matter) with the higher qualities and between 1 and 2% (1·15–2·3% on the dry matter) for the inferior qualities.

* * *

Wheat offals vary so much in size of particle and in chemical composition in different districts that it is almost impossible to give average data concerning them.[1]

Usually the *flour* includes all particles of the milled wheat fine enough to pass through silk sieves (No. 10) with 130 meshes to the linear inch. The residue forms the offals.

The coarser offals are almost universally taken out as *bran*, which is mostly that not passing through a wire sieve with about 16 meshes to the linear inch. The finer offals are commonly separated into three grades, namely, *fine middlings, coarse middlings* and *pollards*, although in some mills it is customary to turn out offals consisting of mixtures of two of the above grades and in some cases all the offals (except bran) are sold together.

The mean percentage compositions of a few samples of different grades of offals are as follows (Wood and Adie) :

[1] Wood and Adie : *Journal of the Board of Agriculture*, 1917, XXIII, pp. 1179 *et seq.*

Table IV

Compositions of Wheat Offals

	Water.	Protein.	Fat.	Carbohy-drates.	Fibre.	Ash.
Fine middlings	12·73	15·75	3·44	63·80	1·86	2·42
Coarse ,,	13·46	16·42	5·03	56·22	5·29	3·58
Pollards . .	13·32	14·39	4·76	55·50	7·70	4·33
Bran . . .	13·63	13·45	3·92	53·12	10·58	5·40

BREAD

Variations in the quality of bread depend essentially on the quality of the flour used, the method of preparation and the degree to which the baking is carried. Wheaten flour, which is that most commonly used for making bread, varies in composition according as the separation of the offals (bran, etc.) is more or less complete. Flour usually constitutes about 80% of the whole of the wheat, but bread may be made of wholemeal or even of meal containing an excess of bran. Other flours are also sometimes used for making bread, either alone or in admixture with wheaten flour.

Bread is analysed mainly to ascertain if it contains any constituent injurious to health. For this purpose a complete analysis would be required, but in most cases the following tests and determinations may be regarded as sufficient: examination of the external and microscopic characters, determinations of the moisture, ash, gluten and acidity, and investigation of extraneous substances (*see* sections 1–6, 9, 13, 14, 15); other subsidiary determinations which may be made are those of the cellulose, fatty substances and nitrogen (*see* sections 8, 10–12). The following are the methods employed:

Sampling.—Whole loaves should be taken, weighed immediately and wrapped in parchment paper, note being made of the time at which the bread left the oven and of that at which the sample was taken.

1. External Characters.—The taste and smell—whether pleasant or not, acid, etc.—are observed. The crumb is also examined to ascertain if it is soft, porous, elastic, homogeneous and adherent to the crust, a lens being used to see if coloured spots or traces of mould occur in it, if it is more or less white, and if the fragments of bran present are more or less numerous.

The colour of a section of the loaf is compared with that of a standard bread.

2. Apparent Density.—The apparent density of the bread, which is intimately related to the volume of the pores, is determined by dividing the weight of a loaf or that of a certain portion of the crumb by its volume; one of the following modes of procedure may be employed:

(1) A whole loaf is weighed, coated with either molten butter or a guttapercha varnish and immersed in a vessel full of water; the water

displaced is collected in another vessel beneath and weighed. The weight of the loaf, divided by that of the water, represents the apparent density of the bread.[1]

(2) A slice of the bread about 2·5 cm. thick is left to dry in the air until it becomes fairly stiff, five or six small cylinders being then cut from it by means of a cork-borer. These cylinders are made all of the same height and dried at 100°, each being afterwards weighed and the mean weight of a cylinder calculated. The mean volume is calculated by multiplying the height by the area of the base, this area being determined from the internal diameter of the cork-borer. Apparent density = mean weight divided by mean volume.[2]

This determination is of value only when the pores are distributed uniformly and when no abnormally large holes are formed during the baking.

3. Microscopic Examination.—This serves to show if a bread is made from wheaten flour alone or if it contains also extraneous flours. The test is made on the crumb, parts which are less well baked being chosen or, if possible, lumps or nodules of dough such as are often present. The fragments taken are made into a paste with water and the microscopic examination then made. A convenient method, which gives excellent results, is as follows :

A piece of the crumb of the size of a pin's head is moistened on a microscope slide with a drop of water and covered with a cover-slip, which is carefully pressed and turned round and round with the tip of the finger. In this way those starch granules which have undergone but little alteration are separated and moved towards the outer part of the preparation, where they may be easily observed. Thus were obtained the preparations for the microphotographs 33 and 34 of Plate V (at end of chapter) ; both were obtained from pure wheaten bread, the former being from a loaf made from 80% flour (i.e., flour containing 80% of the grain) and the latter from a small fancy loaf.

It has been found in practice that wheaten bread of all types always contains a certain quantity of starch granules which have undergone so little alteration that they may be recognised with certainty. Further, wheat starch granules, when deformed by swelling or rupture, never exhibit cavities or fissures similar to those of other granules, e.g., those of rye starch.

It is thus possible to settle microscopically if a wheaten loaf contains rye (but not the converse) or if potato, maize and leguminous starches are present. It is, however, far more difficult to detect in this way the presence of barley, oats or rice, the swollen and deformed starch granules of these being virtually indistinguishable from those of wheaten flour.

In this case also the microscopic examination may be directed to the bran particles, which may be collected directly if the bread is rich in bran ; otherwise the bread is treated with boiling dilute hydrochloric acid, as described for flour (*see* p. 52).

4. Determination of the Crust and Crumb, and Preparation of

[1] Menicanti and Prausnitz : *Staz. sper. agrar. italiane*, 1899, p. 491.
[2] Scala : *Staz. sper. agrar. italiane*, 1899, p. 489.

the Sample for Analysis.—The first determination is that of the respective proportions of crust and crumb. A whole loaf is weighed and separated quickly by means of a knife into crust and crumb, either both or only the former being weighed.

Crust and crumb are then taken in the proper proportions to give a sample of at least 100 grams, this being dried at 100–105° for 2-3 hours and then reduced to a homogeneous powder in a mortar. The powdered sample is kept in a sulphuric acid desiccator and when the various portions required for the different determinations are to be weighed out (the weighings are to be made consecutively and rapidly, in order to avoid absorption of moisture) it is put in the oven again for 2 hours at 100–105°. The samples of crust and crumb separately are prepared in the same way.

5. Moisture.—This is determined either on the whole bread or on the crust and crumb separately. In the former case the loaf, whether round or elongated, is cut into four parts by two cuts at right angles. One part is weighed and then cut into thin slices which, together with any crumbs produced during the cutting, are dried in a tared glass vessel in an air-oven at 105–110° for 7–8 hours, cooled in a desiccator and weighed rapidly on a rough balance sensitive to 0·5 centigram : loss in weight represents moisture.

If the percentage of moisture present when the sample is taken is required, the whole loaf should be weighed at that time and also just before analysis, allowance being made in the calculation for the moisture lost in the meantime.

6. Ash.—This is determined either on the sample prepared as in section 4 (above) or on the crumb alone. The method used varies according as sodium chloride is or is not present, this being ascertained by the taste or by charring about 10 grams of the dry crumb in a platinum dish, lixiviating the charred mass with hot distilled water, filtering, acidifying with nitric acid and testing with silver nitrate : in absence of sodium chloride, the liquid is rendered only slightly turbid. The ash is then determined as follows :

(a) IN ABSENCE OF SODIUM CHLORIDE, 10 grams of the dry bread or crumb prepared as in section 4 are incinerated in a muffle at a low red heat in the manner described in paragraph 6 of the article dealing with flour, and the residual ash weighed.

(b) IN PRESENCE OF SODIUM CHLORIDE, 5 grams of the powdered bread, well dried at 105°, are shaken for some time in a beaker with 30–40 c.c. of cold distilled water, the fragments adherent to the sides of the beaker being washed down with a fine water jet and the whole left to digest overnight. It is then filtered through a rapid ashless filter, the deposit being washed two or three times by decantation with cold distilled water and then transferred completely to the filter, where the washing is continued ; not more than 200 c.c. of liquid should be obtained.

This aqueous extract is evaporated on a water-bath in a moderately large tared *platinum dish*, the liquid being carefully added a little at a time ; when the whole of the solution is evaporated to dryness, the residue is charred *rapidly* over a naked flame and incinerated in a muffle—previously

heated to dull redness—in which the dish is left for *not more than 15 minutes*. The ash is weighed (a) and the sodium chloride (c) in it determined by Volhard's method.

The *residue* left on the filter, after extraction with water, is dried in an oven at 105° and then incinerated in a muffle at a red heat and weighed (b).

The percentage x of ash in the bread is given by : $x = (a + b - c) \times 20$.

This method gives exact and concordant results, which are not obtained by direct incineration or other methods. Indeed, during direct combustion and incineration of the bread, reactions occur between the sodium chloride and the natural components of the bread which result in the evolution of hydrochloric acid and other secondary changes leading to marked alteration of the final results.

The ash determined in the above manner furnishes one of the best criteria for deciding what quality of flour has been used in making the bread. If mineral substances or even so-called baking powder were added to the flour, the ash would show an increase ; in this case, tests 14 and 15 are applied.

7. Nitrogen.—The nitrogen or nitrogenous substances are determined as in flour (*q.v.*, section 17).

8. Gluten.—100 grams of the bread (crust and crumb in proper proportions) are moistened with water and left for about half an hour to swell up thoroughly ; the moist dough is then placed on a very fine sieve and manipulated under a water jet in the way described for the separation of gluten from flour (*q.v.*, section 7).

9. Fatty Substances.—These are determined on the sample of bread prepared as described in section 4.

The fatty substances cannot, however, be removed completely from bread by the direct extraction used in the case of flour, the following procedure being necessary.

5 grams of the bread or crumb are treated, in a reflux apparatus of about 200 c.c. capacity placed on a boiling water-bath, with 25 c.c. of approximately N/2-hydrochloric acid, the flask being frequently shaken during the course of 20 minutes. When cold, the liquid is shaken with 5 c.c. of ammonia (D 0·96) and 20 c.c. of 90% alcohol and transferred to a separating funnel together with a mixture in equal volumes (about 100 c.c.) of ether and petroleum ether, the flask being well rinsed out with the same mixture of solvents. The whole is repeatedly shaken and left to separate into two layers, the aqueous liquid being drawn off and the ethereal solution washed with water and filtered through a small filter into a tared dish ; the latter is left until the solvent evaporates and then dried for an hour in a steam-oven and weighed. Weight of residue, multiplied by 20, gives the percentage of fatty substances.

This determination is useful in deciding if a bread has been either prepared with addition of fatty materials, e.g., butter, or baked in a vessel lined with fat (lard, dripping, etc.) ; in either case the fatty substances would show an increase relatively to that naturally contained in bread.

10. Cellulose.—This is determined by one of the methods given for flour (*q.v.*, section 15), preferably by that of König, the sample of bread prepared as described in section 4 being used.

11. Sugars and Dextrin.—10 grams of the dry powdered bread are shaken for some time in a 500 c.c. measuring flask with about 400 c.c. of distilled water at the ordinary temperature, the liquid being then made up to volume and filtered. On an aliquot part of the filtrate the sugars and dextrins are determined as described for flour (*q.v.*, section 16).

The use of any substance with a maltose basis, for the purpose of facilitating the rising, will increase the saccharine substances.

12. Acidity.—2 grams of the dry, powdered bread are treated in a 500 c.c. flask with about 300 c.c. of water which has been boiled for some time and is still boiling. The flask is shaken at frequent intervals until the liquid is cold, boiled water being then added to the mark and the whole well shaken, left for a time and afterwards filtered ; 250 c.c. of the filtrate (corresponding with 1 gram of the bread) are titrated with N/10-potassium hydroxide in presence of phenolphthalein.

The acidity is expressed in c.c. of N-KOH per 100 grams of dry bread or in per cent. of sulphuric or lactic acid (1 c.c. N-KOH = 0·049 gram H_2SO_4 or 0·090 gram $C_3H_6O_3$).

13. Extraneous Mineral Substances.—Addition of extraneous mineral substances, such as gypsum, calcium carbonate, alum, heavy metals, etc., is detected as in flour (*q.v.*, section 12), and a similar method serves for the detection of sand and soil resulting from the imperfect cleaning of the grain employed.

14. Substances added to facilitate Working.—These substances are added either to aid the rising of the dough or to give artificially greater volume to the bread. Among the former are diamalt and other malt preparations, while the latter include so-called baking powders, which usually consist of sodium bicarbonate mixed with tartaric acid (or cream of tartar) and a little corn flour.

Addition of substances of the former class may be detected by the increased proportion of saccharine substances in the bread when the added sugar has not been entirely decomposed.

Powders with a tartaric acid basis are tested for as follows : About 20 grams of the powdered bread are treated with water in a flask of about 200 c.c. capacity on a water-bath, the liquid being concentrated to about 50 c.c., transferred to a separating funnel, acidified with sulphuric acid and extracted with ether. The ethereal solution is evaporated in a porcelain dish and the residue heated with a few crystals of resorcinol and one or two drops of concentrated sulphuric acid until white fumes appear : the formation of a violet-red coloration indicates the presence of tartaric acid.

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Good bread should have a pleasant odour and a crust which is brownish, shining, uniform and adherent to the crumb. The latter should be more or less white (according to the extent to which the offals are separated), soft, elastic, porous, homogeneous, free from spots, and of pleasant, non-acid taste.

The proportions of *crust and crumb* depend on the shape and size of the loaf and vary from 22 to 45% and from 78 to 55% respectively. The crust varies in thickness and is 4–5 mm. thick in bread made from an 80% flour.

The *density* of bread is somewhat variable and is related to the volume of the pores, being small in very porous loaves and higher in those which are more compact ; in general the quality and digestibility of a bread increase with the lightness and porosity.

Microscopic examination should not reveal in wheaten bread any extraneous elements or flours of injurious seeds.

The *moisture* content of bread is very variable and increases with the volume of the loaf ; in bread well made and well baked and of the usual size and shape it should not exceed 30–35%.

The *ash*, referred to 100 parts of dry bread, corresponds with that present in the flour (dry) employed.

The amounts of *cellulose, fatty substances*, and *nitrogenous matters* are related to the proportions of these substances present in the flour.

The *acidity* of bread usually lies between 0·1 and 0·4%, expressed as sulphuric acid.

MACARONI, VERMICELLI, ETC.

These materials are usually made from the flour of hard wheat (grano duro) and their quality depends on that of the flour.

The complete analysis comprises determinations of the moisture, ash, gluten, nitrogen, fat, cellulose, digestible carbohydrates and acidity. All these determinations are made on the finely powdered material by the methods described for flour. The following investigations are also of importance.

1. External Characters.—The taste and smell are noted to ascertain if there is any rancidity or mouldiness ; also the colour : whether yellowish, whitish or grey ; the outer appearance : whether uniform or otherwise ; the appearance of the fracture : whether vitreous or floury. No trace of mould or parasites should be observable, either by the naked eye or with the aid of a lens.

2. Boiling Test.—50 grams of the substance are boiled for 20 minutes in 500 c.c. of water containing 2·5 grams of salt. The appearance of the material—whether split or jellified or not—and that of the water—whether more or less milky and containing more or less sediment—are observed.

3. Microscopic Examination.—The substance is well powdered and left to digest in water for some time, with occasional shaking ; it is then examined under the microscope as in the case of flour (*see* p. 50).

The extraneous flour most commonly used as an adulterant of these materials is that of maize, recognisable by its polygonal starch granules, although these are not always so characteristic as in the flour, many of them being deformed, especially when the maize in question has been subjected to the action of heat. Careful examination will, however, always reveal some maize starch granules with their original form ; comparison with a sample of similar material known to contain maize is useful. Fig. 35 of Plate V (at end of chapter) represents material made from pure wheat, and Fig. 36 a preparation containing wheat and maize.

Potato flour, rice flour and others are also used, but only rarely.

4. Detection and Determination of Eggs.—The procedure is as follows :

(*a*) QUALITATIVE. The physical examination is often sufficient to indicate the presence of egg, owing to the characteristic taste and yellow colour of the latter (absence of artificial coloration is assumed). The following tests may also be made.

1. The finely ground material is heated in a reflux apparatus with petroleum ether and ammonium carbonate, the mass being afterwards filtered and the petroleum extract shaken with methyl alcohol. The latter is separated and evaporated on a water-bath : the presence of egg is then detectable by the odour of the residue.

2. The fat, determined in the ordinary way, is increased by the presence of eggs.

3. The iodine number is determined on the fat extracted from a sufficient amount of the substance (at least 100 grams) : the iodine number of the oil of wheat is above 100, whereas that of egg fat is about 70–80.

The iodine number of the fat contained in egg is variable, a gradual diminution occurring, so that it gives a definite positive indication only with material which has been recently prepared. A high iodine number, however, is certain proof of the absence of egg.

(*b*) QUANTITATIVE. This is based either on determination of the phosphoric acid of the lecithin (which amounts to 0·02–0·03% when egg is absent, but is greater when egg is present), or on estimation of the cholesterol, which is found only when eggs have been used.

1. *Determination of the Phosphoric Acid of the Lecithin.* 35 grams of the finely ground material are extracted for 12 hours with absolute alcohol in a Soxhlet apparatus. The alcohol is evaporated and the residue taken to dryness with 5 c.c. of 20% potassium hydroxide solution and then incinerated. The phosphoric acid in the ash is determined and calculated on 100 parts of the dry material.

To obtain the number of eggs from the phosphoric acid of the lecithin use is made of the following table :

Percentage of Phosphoric Acid in the Dry Substance.	Number of Eggs added to 100 grams of Flour.	Percentage of Phosphoric Acid in the Dry Substance.	Number of Eggs added to 100 grams of Flour.
0·0513	1	0·1744	6
0·0786	2	0·1954	7
0·1044	3	0·2155	8
0·1289	4	0·2348	9
0·1522	5	0·2531	10

The results obtained in this way are only approximate, since the compositions of flour and eggs vary, although within definite limits ; the above table is based on mean values.

2. *Determination of the Cholesterol.* From 400 to 500 grams of the powdered material are extracted with anhydrous ether, the latter being then distilled off, the residue saponified with alcoholic potash and the solu-

tion of the soap evaporated to dryness. The residue then remaining is again treated with ether and the ethereal solution filtered. The substance left on the filter is treated with hot methyl alcohol and the hot alcoholic solution filtered, mixed with 20% of water and evaporated to incipient crystallisation. The liquid is cooled to 0°, this causing the crystallisation of all the cholesterol, which is collected on a tared filter, washed with 50% methyl alcohol solution and then with hot water and dried at 100° to constant weight (2–3 hours). The quantity of cholesterol in an egg is 0·17–0·25 gram.

5. Extraneous Colouring Matters.—Most of the products in question are coloured a more or less deep yellow by means of organic colouring matters or, sometimes, saffron, the depth of colour depending on whether enhancement of the natural colour of the flour or imitation of the colour imparted by eggs is desired. In Italy the use of picric acid, Victoria yellow, Martius yellow and metanil yellow for this purpose is prohibited.

Possetto's method of testing [1] is as follows : To 250 c.c. of boiling water contained in a porcelain dish are added first 20 c.c. of 95% alcohol and 2 c.c. of 10% ammonia solution and immediately afterwards 30 grams of the material. After about 5 minutes' boiling—when it is considered that the liquid is sufficiently coloured—cold water is added and the solid allowed to settle. The liquid is decanted into another dish and, after slight acidification with 10% hydrochloric acid, a small skein of defatted wool (0·5 gram) boiled in it for 10 minutes. If the wool remains yellow after repeated washing with water, the presence of a coal-tar colour is indicated.

To ascertain if one of the above prohibited colours has been employed, the dyed wool is boiled for 5 minutes in a beaker with 50 c.c. of water rendered slightly alkaline with ammonia. The latter dissolves the colouring matter, the nature of this being then determined by means of the tests indicated in the table given by Possetto (next page).

6. Extraneous Mineral Matters.—Tests should be made for heavy metals (copper, lead, zinc, etc.) and for alum, which is sometimes added, together with sodium bicarbonate, to prevent acidification (*see* Flour, section 12).

* * *

If of *good quality*, the material has a pleasant smell and taste (not mouldy or rancid), a yellowish colour, a uniform external appearance and a vitreous fracture. It should also resist fracture and pressure by the fingers and should be in a state of perfect preservation.

It should withstand the *boiling test* for not less than 20 minutes without splitting or breaking down, the water showing only a slight floury sediment.

The proportion of *water* present should not exceed 13–14%.

The percentage of *ash* corresponds with that of the flour used in the manufacture and in the first and second qualities is usually below 0·7 and 1·0 respectively ; dark products, made from inferior flours, contain more than 1%.

The amounts of *fat, cellulose, nitrogenous matters, sugars* and *starch* are also related to the amounts in the original flour. Products containing added *gluten*

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[1] G. Possetto : *Giorn. Farmacia e Chimica, etc.*, 1914, p. 390.

TABLE V

Systematic Examination of the Yellow Organic Dyes in Macaroni, etc. (Possetto)

If the aqueous solution of the yellow dye is not decolorised by HCl and SnCl₂, the four prohibited colouring matters are excluded. If decolorisation or reduction occurs, a few drops of ferric chloride are added. The reappearance of the original colour also excludes the four dyes mentioned. If the colour does not reappear, the colouring matter (if yellow) can only belong to either the (A) Nitro- or (B) Azo-colouring matters.

(A) Nitro-colouring Matters :

Yellow or orange colouring matters soluble in water without fluorescence. The aqueous solution is decolorised or precipitated by HCl, but is not altered by KOH. Reduction at a gentle heat with a little HCl and SnCl₂ gives nitroamines, colourless compounds turned red by alkalies (nitro-phenols). The nitroamines are coloured red by reduction.

The aqueous solution of the colouring matter acidified by acetic acid and extracted with ether gives :

Yellow ethereal solution able to give up its colour to ammonia
→ Non-sulphonated nitro-phenols (Picric acid ; Victoria yellow ; Martius yellow)

Yellow ethereal solution incapable of yielding its colour to ammonia
→ *Nitroamines* (e.g., Aurantia)

Colourless ethereal solution yielding nothing to ammonia
→ *Sulphonated nitro-phenols* (e.g., Naphthol yellow S)

The aqueous solution of the colouring matter is treated with :

Cold HCl	Solid KCN for 5 minutes on a boiling water-bath	
Slight discolorisation without precipitation	Reddish-brown coloration	*Picric Acid*
Much decolorisation and yellowish-white precipitate	Orange-red coloration (yellow with acetic acid)	*Victoria yellow*
Almost complete decolorisation with yellowish-white precipitate	Orange-red coloration (bluish-green with acetic acid)	*Martius yellow*

(B) Azo-colouring Matters :

Colouring matters with various colours mostly soluble in water. They dye silk and wool directly

If the aqueous solution is orange yellow ; if it assumes a fuchsine-red colour on treatment with HCl ; if it gives a violet colour when evaporated to dryness and then taken up with concentrated sulphuric acid ; if this sulphuric acid solution changes to fuchsine-red on dilution ; if it dyes wool in an acid bath
→ *Metanil yellow*

76

—for the use of persons suffering from diabetes—should be far richer in nitrogen than the ordinary materials, but this is not always found to be the case.

The *gluten* obtained from these substances should be yellowish-white or pale grey, glossy, of good odour, tenacious and elastic, and easy to extract.

The *acidity* should not, as a rule, exceed 0·1% as lactic acid or 0·054% as sulphuric acid, in products of the first grade; it may be as high as 0·3% as lactic acid or 0·16% as sulphuric acid in second grade materials.

STARCHES

Starch is obtained from cereals, from leguminous and other seeds, from potatoes and other tubers, and from certain roots. The starches which are most commonly used are those of wheat, maize, rice, potatoes, sago, manioc and maranta.

Analysis of starches (especially those of wheat, maize, rice and potatoes) is made principally to determine their purity, that is, to ascertain if they have been more or less completely freed from the other substances which accompany the starch in the seeds, tubers or roots, such as nitrogenous substances, woody matter, mineral salts, etc.

To this end the following tests and determinations are made.

1. Microscopic Examination.—This serves for the recognition of the nature of a starch. The characters of starch granules of different origins are described in the chapter on flour (p. 53).

2. Moisture.—10 grams of the starch, in a flat metal dish about 75–85 mm. in diameter, are heated in an air-oven for an hour at 40–50°, the temperature being then raised to 120° in half an hour and maintained at this point for 4 hours. The loss in weight represents moisture.

3. Ash.—10 grams of the starch are charred over a direct flame and then incinerated in a muffle at a dull red heat.

If the proportion of ash exceeds the limits given at the end of this article, the product is inferior or has been adulterated with mineral substances, such as gypsum, chalk, talc, etc., which may be detected by qualitative analysis of the ash.

4. Acidity.—Qualitative. A small portion of the starch, slightly compressed by means of a flat surface, is treated with 1–3 drops of tincture of litmus diluted to a garnet-red colour. If a blue or dark violet coloration is formed, the starch is free from acid, whereas a brick-red colour denotes marked acidity.

QUANTITATIVE. The acidity is estimated as follows: 25 grams of the product are made into a paste with 30 c.c. of water and titrated, with shaking, with N/10-caustic soda solution until a drop of the starch suspension, when placed on a filter-paper folded several times so as to absorb the water, is no longer coloured red by tincture of litmus. The acidity is expressed in c.c. of decinormal alkali per 100 grams of starch.

5. Determination of the Nitrogen.—This is determined as in flour (*see* p. 65). The presence of gluten is detected by the abundant and persistent froth formed when 1 gram of the starch is boiled and shaken with 180 c.c. of water; the cereal origin of the starch is thus shown.

6. Determination of the Cellulose.—As in flour (*see* p. 62).

7. Investigation of the Impurities.—Commercial starches some-times contain extraneous mineral matters, such as sand, gypsum, chalk, baryta, alumina, etc., as well as foreign organic substances, e.g., bran, potato residues, fungi, algæ, sacking fibres, fragments of roasted starch, etc.

The presence of extraneous *mineral matters* is detected as follows : 4–5 grams of the powdered substance are shaken in a test-tube with chloroform and then left to stand ; any mineral matter then settles at the bottom of the tube, whilst the starch floats at the surface of the liquid. Analysis of the ash of the product by the ordinary methods indicates the nature of the inorganic substances.

Foreign *organic substances* may be readily observed if the starch is spread out on a sheet of paper and the surface, smoothed by means of a glass plate, carefully examined with the naked eye or, better, with the aid of a lens ; the various impurities appear as black, brown or otherwise coloured spots on the white surface of the starch. The number of such spots per sq. dm. may be determined, the mean of several (at least five) countings being taken.

8. Detection of Dextrin.—A certain quantity of the product is shaken with cold water and filtered : in presence of dextrin the filtrate will be dextro-rotatory and will be coloured reddish by a solution of iodine in potassium iodide.

9. Pasting Test.—The ability of a starch to form a stiff, homogeneous paste with water may be tested as follows :

4 grams of the starch are well mixed with 50 c.c. of water in a porcelain dish, which is then heated *directly* over a bunsen flame while the mass is stirred with a glass rod. The burner is removed when the paste becomes transparent and begins to froth, the stirring being continued for some little time, after which the mass is left to cool. The duration of the cooling should not exceed one minute. The cold paste should be homogeneous and should not pour out when the dish is inclined.[1]

10. Technical Tests.—To ascertain the suitability of a starch for use in the dressing of textiles, samples of fabrics dyed with sensitive colours (benzopurpurin, Turkey red, logwood black) or of bleached fabrics are treated with the starch ; the dry materials are examined as regards feel and change of colour, while the general appearance is compared with that of the same material dressed with a standard starch.

This test is usually made in the works or in special laboratories.

* * *

Starches contain varying proportions of water, the normal content being 14–18% (18–20% is allowable). *Green starch*, which is the manufactured starch prior to drying, usually contains 48–53% of water.

The *ash* in starches of good quality should be less than 0·5% (the finer brands show 0·05–0·3%) ; inferior starches contain rather more, but usually below 1%.

As regards the *acidity* : a starch is described as feebly acid, acid, or strongly

[1] P. Heermann : *Färbereichemische Untersuchungen* (Berlin, 1907).

acid, according as 100 grams require less than 5 c.c., from 5 to 8 c.c., or more than 8 c.c. of decinormal caustic soda for neutralisation.

The *nitrogen* in ordinary starches may amount to as much as 0.7% on the dry substance, but the finer qualities contain either no nitrogen or only a very small proportion (not more than 0.15%).

Cellulose should be present in starches only in traces—not above 0.3% at the most.

The number of *spots* (impurities) in fine starches varies from 15 to 28 per sq. dm., in ordinary starches from 145 to 148, and in inferior qualities from 700 to 800. As few as possible should be present in starches for use in the manufacture of fine white papers or in the dressing of white or pale coloured fabrics.

DEXTRIN

This results from the transformation of starch by means of heat or by the action of dilute acid or diastase. It is prepared principally from potato, wheat or maize starch and rarely from rice or other exotic starches. Many varieties of dextrin, made in diverse ways, are sold under different names. It occurs as a fine powder, either white, dirty white, yellowish or light brown; as granules, similar in appearance to gum arabic; and as a thick syrup, more or less highly coloured and opaque. In general dextrin has a special odour and taste, which are particularly marked in the pulverulent varieties. It is soluble in water, but insoluble in alcohol. Its solution is strongly dextro-rotatory; the value of $[a]_D$ varies from 123° to 225°, but is mostly about 200°. With iodine different dextrins give bluish violet to brownish red colorations (the colour is observed by adding the iodine solution drop by drop; if the mass is mixed after the first drops are added, the colour disappears).

Analysis of commercial dextrins, with the view of determining their purity and their value for various industrial purposes, includes the following investigations:

1. External Characters.—The colour, odour and taste are to be noted. White or yellow dextrins are mostly prepared by means of acid (hydrochloric acid tends to give a reddish and nitric acid a greyish tint), whereas brown dextrins are those obtained by direct torrefaction without acid.

The best dextrins, derived from good potato starch, exhibit a shining reflection, those which appear opaque being usually obtained from wheat or maize starch.

The material should be examined to ascertain if the colour is homogeneous, brown spots or stains being an indication of faulty manufacture or inferior raw materials.

The smell is slight with the dry dextrin, but is brought out on moistening with water; no odour of mould should be detectable.

A more or less acid or sweetish taste denotes the presence of acid or saccharine matter.

2. Microscopic Examination.—Dextrin prepared by heating retains the structure of the original starch to a sufficient extent to permit of its origin being determined by microscopic examination in oil or glycerine (not in water): *see* Fig. 37 of Plate V at end of chapter.

3. Moisture.—10 grams of the substance are kept in an oven at 105° for 4 hours and then reweighed : loss of weight represents the water present.

4. Acidity.—100 grams of the dextrin are treated with about 800 c.c. of boiling water and the solution titrated in the cold with normal caustic alkali either in presence of phenolphthalein or, with a coloured solution, with the help of litmus paper. The acidity is expressed in c.c. of normal alkali per 100 grams of substance.

5. Ash.—10 grams of the substance are incinerated in a platinum dish, the last traces of carbon being treated with ammonium nitrate and again calcined and the residue weighed. This residue is then treated with hydrochloric acid, any insoluble remainder (sand) being well washed with water, ignited and weighed.

6. Matter soluble and insoluble in Cold Water.—The matter *soluble* in cold water is determined by treating 30 grams of the substance with 300 c.c. of distilled water at 17.5°, the mass being well shaken until all lumps have completely disappeared and then filtered ; 5 c.c. of the filtrate are weighed in a tared dish and evaporated to dryness, the residue being dried at 105° for 4 hours and its weight multiplied by 200 to obtain the percentage of soluble matter in the dextrin. The *insoluble* matter is determined by difference.

The white dextrins are the least soluble in cold water, the insoluble part consisting of soluble starch and of more or less marked proportions of organic (cellulose, gluten, etc.) or mineral impurities (sand).

7. Matter soluble and insoluble in Hot Water.—A few grams of the dextrin are boiled with distilled water and the *insoluble* matter collected on a tared filter, washed, dried at 105° and weighed. The *soluble* matter is determined by difference.

As a rule, dextrins are almost completely soluble in hot water, the insoluble matter being composed of a few organic impurities (cellulose, gluten) together with a little sand. Sometimes, however, they contain untransformed starch, which is due to faulty manufacture or is added intentionally and is found in the residue insoluble in hot water.

8. Determination of the Dextrin.—The content in dextrin may be determined either indirectly or directly.

(*a*) INDIRECT METHOD. In an aliquot part of the aqueous solution prepared in the cold (*see* section 6, above) the reducing substances are determined (*see* section 10, below), and in another part the ash is determined. The percentage of matter soluble in cold water, less the percentages of reducing substances and ash, represents the pure dextrin present.

(*b*) DIRECT METHOD. This is based on the solubility of dextrin in dilute alcohol and in its insolubility in concentrated alcohol. The aqueous solution (prepared in the cold) of a weighed quantity of dextrin is evaporated to a syrup, which is then mixed with ten times its volume of 90% alcohol, the precipitated dextrin being collected on a filter, washed with 90% alcohol and dried. 1 gram of this dextrin is dissolved in 10 c.c. of water and the solution treated with 30 c.c. of 56% alcohol, 4 drops of 26% ferric chloride solution and about 0.5 gram of powdered chalk. The whole is well

shaken and filtered and the insoluble part washed with 56% alcohol, the filtrate—which contains the pure dextrin in solution—being treated with sufficient 96% alcohol to precipitate all the dextrin. After 24 hours the alcohol is decanted off, the dextrin remaining behind dissolved in a little water, the aqueous solution evaporated in a tared dish and the residue dried at 105° and weighed.

9. Determination of the Starch.—Dextrins usually contain soluble starch, i.e., starch soluble in hot (but not in cold) water. Thus, the proportion of starch (soluble) present is represented simply by the difference between the percentages of the matters soluble in cold and hot water respectively. If unconverted starch is also present, this will be found in the residue insoluble in hot water (*see* section 7, above) and may be determined therein by transforming it into sugar (*see* Flour, section 16, p. 63).

The presence of unconverted starch may be detected also by treating the dextrin with concentrated caustic potash solution, which gives a clear solution if only soluble starch is present, but a kind of paste if unmodified starch remains.

10. Determination of the Sugars.—This is carried out by means of Fehling's solution in a portion of the solution of the dextrin in cold water, the ordinary conditions being followed (*see* chapter on Sugars).

The proportion of sugars (dextrose, maltose) in dextrin can be determined only approximately, owing to the presence of a series of products intermediate to dextrin and the sugars and possessing reducing properties towards Fehling's solution. Thus, analysis gives only the amount of reducing substances, this being expressed in terms of dextrose for the sake of convenience.

11. Determination of the Consistency and Stability of the Concentrated Solution.—30 grams of the dextrin are boiled, in a porcelain basin over a naked flame, with 30 c.c. of water, the mass being stirred continuously until perfectly homogeneous. The solution is examined when cold as to consistency and after some days to ascertain if it has remained pasty or has become dry. It is well to make the test in comparison with standard dextrins.

For dressing textiles and for use in the dyeing industry dextrins are preferred which form solutions capable of remaining pasty for a long time.

12. Measurement of the Viscosity.—This can be carried out either on the solution prepared in the cold or on that prepared in the hot. In the former case, 100 grams of the dextrin are shaken with 500 c.c. of distilled water at 17·5° until the whole of the soluble part has dissolved, the liquid being filtered through a dry filter and the filtrate tested in the Engler viscometer (*see* Vol. I, p. 352). In the second case, the solution is prepared in the hot and the viscosity measured when cold. The value obtained is compared with that given by a standard dextrin under the same conditions.

13. Test for Chlorine.—This is made on the aqueous solution by means of the usual reagents, e.g., a paper steeped in potassium iodide. If chlorine is present, a drop of the solution will colour the paper violet or reddish.

The presence of free chlorine or of hypochlorous acid in dextrin may result

from the use of starch bleached with chlorine or from the employment of chlorine in the manufacture of the dextrin.

14. Test for Gluten.—One part of the dextrin is made into a paste with one part of water at 60°, the paste being then diluted with 5 parts of water at the same temperature and left for 24 hours. In presence of gluten, a glutinous deposit forms at the bottom of the vessel.

Marked quantities of torrefied gluten are found in dextrins prepared by the action of heat on inferior wheat starch. In some cases the gluten occurs as small, hard lumps.

15. Technical Tests.—In the case of dextrin for use in the dyeing and printing of textiles, a practical test may be required, this being carried out in the following ways : [1]

(*a*) A piece of perfectly white, pure wool is treated with the following mixture and then steamed, washed and dried, the colour being then noted.

Ammoniacal cochineal solution containing 30 grams of cochineal per litre . . .	1 litre
Powdered alum	24 grams
Oxalic acid	10 ,,
Dextrin	375 ,,

(*b*) Cotton is treated with the following mixture :

Aluminium acetate prepared with 36·5 grams of alum per litre of water	1·32 litres
Water	15·32 ,,
Dextrin	150 grams

The cotton is then dyed with alizarin and the colour observed.

* * *

A *good dextrin* should be of uniform colour without black spots and should have the characteristic odour and no smell of mould. It should be wholly soluble in water, should not give an appreciable reduction of Fehling's solution in a short time, and should not contain gluten or free chlorine in appreciable quantity.

The amount of *water* in commercial powdered dextrins usually varies from 8 to 12%, only products recently prepared containing less than 8%. A higher proportion than 12% is abnormal.

The *acidity* of commercial dextrins should not surpass 5 c.c. of normal alkali per 100 grams.

Good dextrins of the first quality should not leave on combustion more than 0·5% of *ash* and not more than 0·2% of sand ; ordinary dextrins should contain not more than 0·8–1% of ash. Higher proportions of ash and sand indicate either that the dextrin is of lower quality or that it has been prepared from inferior starch or adulterated with mineral matter (rare).

Good dextrins for printing should give on wool (Test 15, *a*, above) a good pink tint quite free from yellow and on cotton (Test 15, *b*) a bright pink tint.

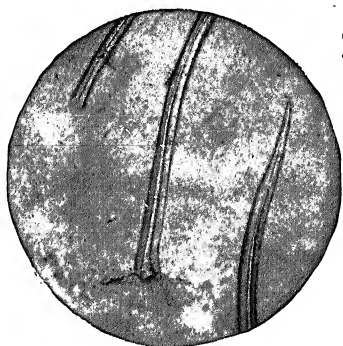[1] A. Bolis : *Ind. tessile e tintoria*, 1903, p. 117.

PLATE I.

FIG. 9.—Wheat hairs.
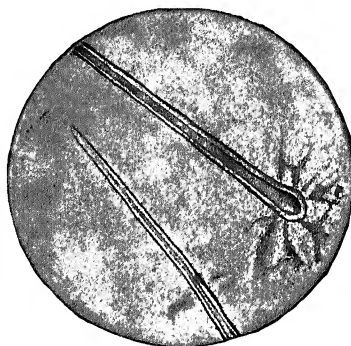
FIG. 10.—Rye hairs.
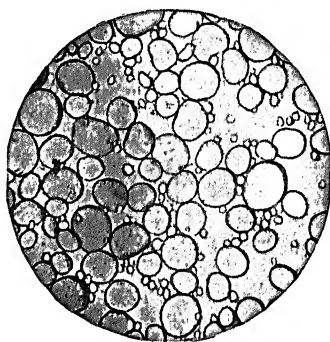
FIG. 11.—Wheat starch.
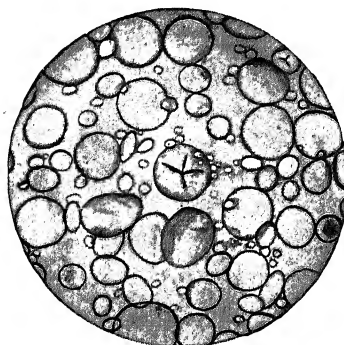
FIG. 12.—Rye starch.
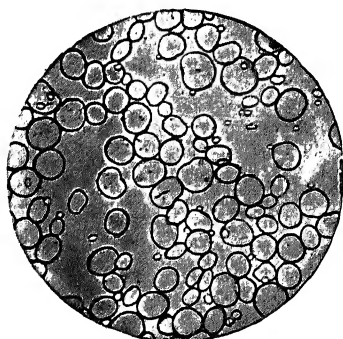
FIG. 13.—Barley starch.
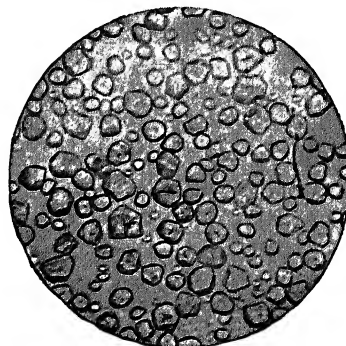
FIG. 14.—Maize starch.

PLATE II.
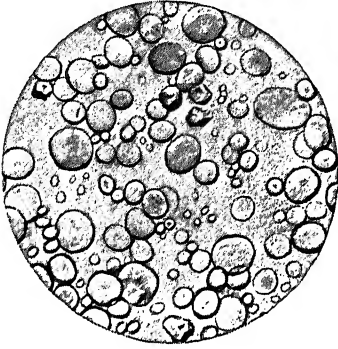
FIG. 15.—Mixture of wheat and maize starches.
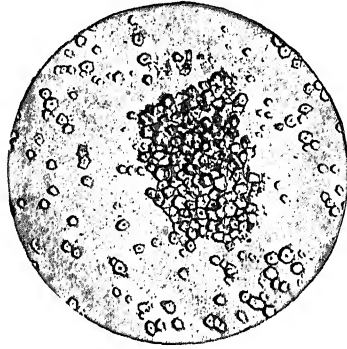
FIG. 16.—Buckwheat starch.
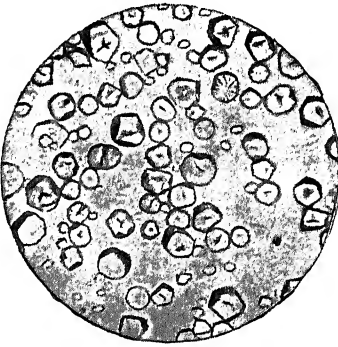
FIG. 17.—Dhurra starch.
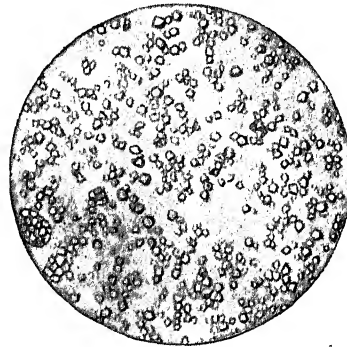
FIG. 18.—Rice starch.
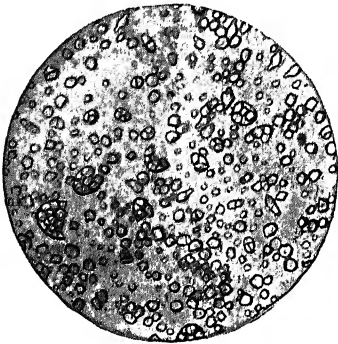
FIG. 19.—Oat starch.
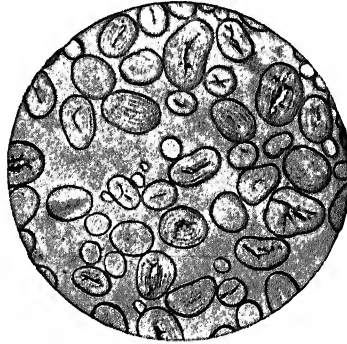
FIG. 20.—French bean starch.

PLATE III.
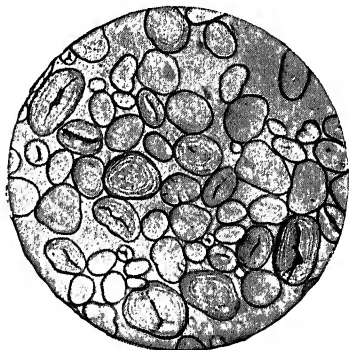
FIG. 21.—Broad bean starch.
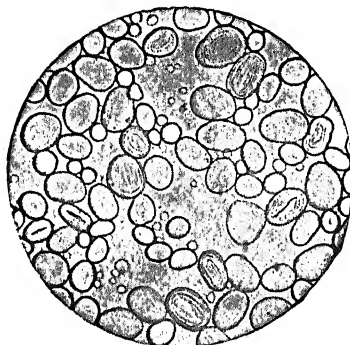
FIG. 22.—Chick peas starch.
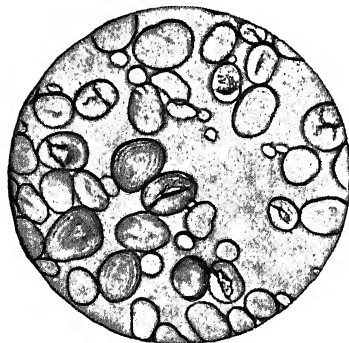
FIG. 23.—Pea starch.
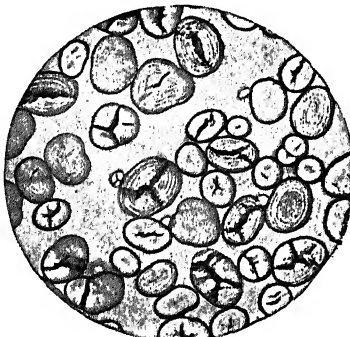
FIG. 24.—Lentil starch.
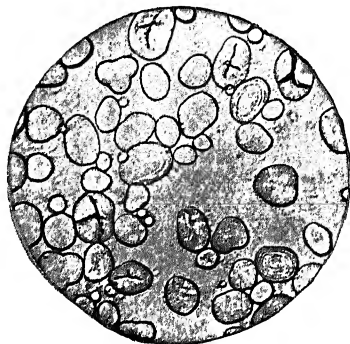
FIG. 25.—Vetch starch.
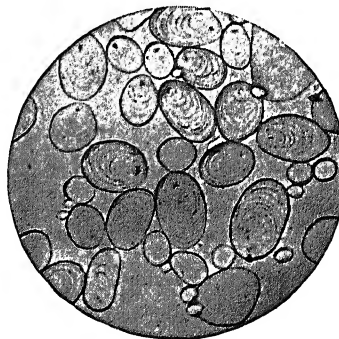
FIG. 26.—Potato starch.

PLATE IV.
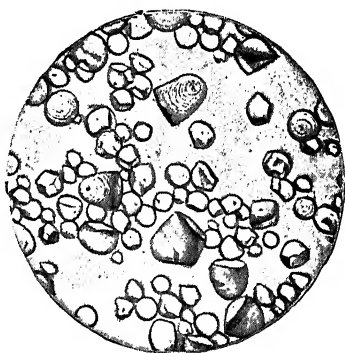
FIG. 27.—Sweet potato starch.
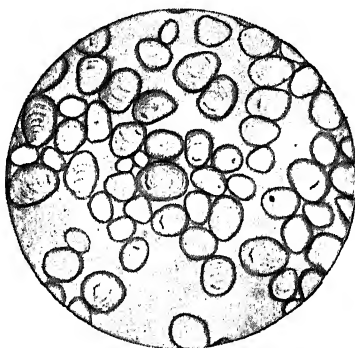
FIG. 28.—Maranta (arrowroot) starch.
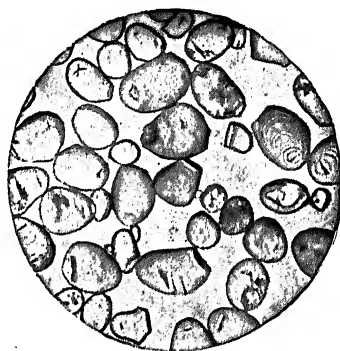
FIG. 29.—Sago starch.
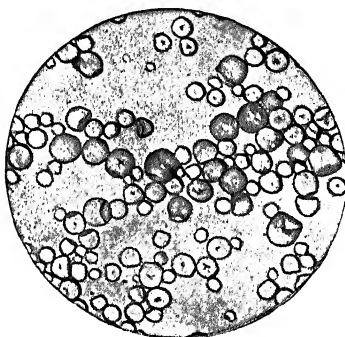
FIG. 30.—Manioc starch.
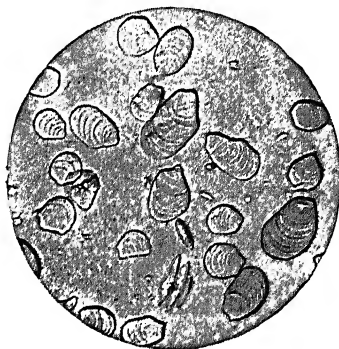
FIG. 31.—E. Indian arrowroot starch.
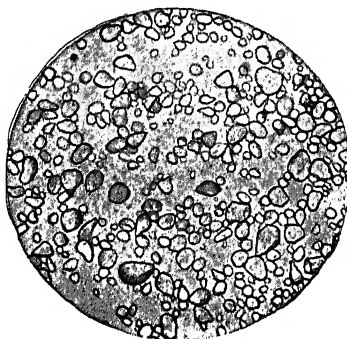
FIG. 32.—Chestnut starch.
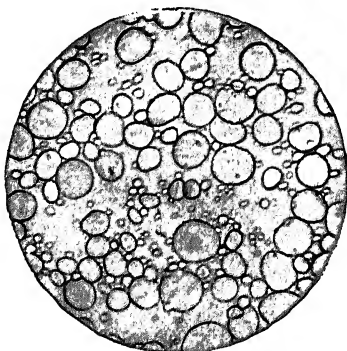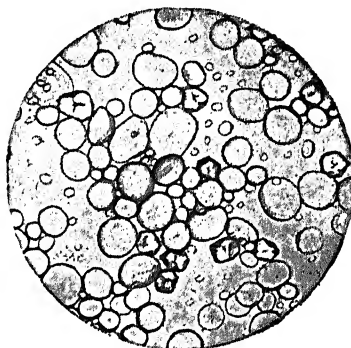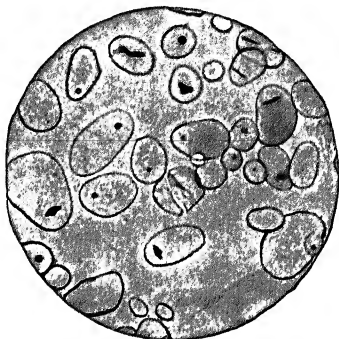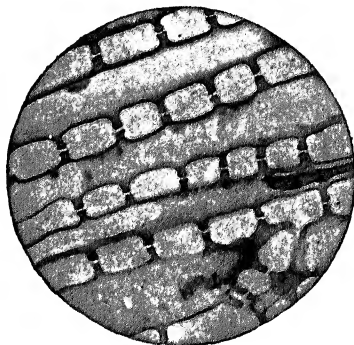
Chapter IV

SUGARS

AND PRODUCTS CONTAINING THEM

The sugars occurring in commercial products are principally saccharose, invert sugar, glucose, levulose and, less frequently, maltose, lactose and raffinose.

The methods employed to determine these sugars in products containing them are in many cases the same, and they are consequently given below in the first part (*General Methods*). The second part (*Special Part*) contains special indications and methods regarding each particular saccharine product.

GENERAL METHODS

The general methods for the determination of sugars are mainly four in number. The first is the *hydrometric method*, based on the relation between the concentration of saccharine solutions and their specific gravity. The second the *refractometric method*, based on the relation between refractive index and concentration of the solutions. The third the *polarimetric method*, based on the rotatory power towards polarised light exhibited to a greater or less degree by sugars. The fourth, the *chemical method*, based on the reducing powers exerted by various sugars on alkaline copper solutions.

A detailed description is given of these methods in so far as they serve for the determination of the individual sugars,[1] their application to the analysis of mixtures of several sugars being then considered.

1. Hydrometric Method

1. Determination of the Specific Gravity.—The specific gravity of saccharine solutions is determined, at a certain normal temperature, by

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[1] It must be pointed out that the hydrometric and refractometric methods are often applied to determine, in liquids containing sugars, the total solid substances (dry matter, extract), considered as if they were wholly sugar. In such cases the results have naturally a purely conventional character.

one of the usual methods for the determination of the specific gravity of liquids, i.e., with a hydrometer, Westphal balance or picnometer (*see* Spirits and Liqueurs).   As regards the use of the hydrometer, the reading is usually made with the eye at the level of the plane surface of the liquid and not at the upper part of the capillary meniscus or edge formed by the liquid with the stem of the instrument.   Only for very dark liquids, such as certain beet-juices, are densimeters sometimes graduated so that they must be read at the top of the meniscus.   As regards the Westphal balance, it is to be noted that it gives uncertain results with very dense solutions, which impede its oscillations.   The picnometric method takes longer, but is more exact and is used particularly as a control or where only small quantities of liquid are available.

As a result of decisions of International Congresses of Applied Chemistry, among them that held at Paris (1900) and of the International Commission for Standard Methods of Sugar Analysis, the specific gravity of saccharine solutions should be determined at 20° C. and referred to water at 4° (sp. gr. at 20°/4°), i.e., it should indicate the weight of a *true* c.c. of solution at 20°.   Use is, however, largely made in practice of the sp. gr. at 17·5°/17·5° and sometimes at 15°/15°.

When a picnometer is used, the sp. gr. at 17·5°/17·5° or 15°/15° is the ratio of the weights p and p^1 of the solution and water respectively.   In determining the sp. gr. at 20°/4°, it must be borne in mind that 100 *true* c.c. of water at 20° weigh 99·7174 grams (weighed in air with brass weights).   Thus, if the capacity of the picnometer is exactly 50 c.c. at 20°, the water it holds at 20° will weigh 49·859 grams and in this case the weight of the sugar solution it contains should be divided by 50 to obtain the sp. gr. at 20°/4°; or, if the picnometer holds a weight p^1 of water at 20°, the weight of water at 4° which would be contained in the same volume will be $p^1/0·997174$, so that the sp. gr. at 20°/4° will be 0·997174 p/p^1.

2. Calculation of the Saccharometric Degree from the Specific Gravity.—By means of suitable tables, the specific gravity gives the saccharometric degree or the concentration.   The case to which the hydrometric method is usually applied is that of saccharose solutions; the saccharometric degree may be expressed with reference either to *weight* (grams of sugar in 100 grams of solution, or percentage by weight, termed also *Balling* or *Brix degrees*) or to *volume* (grams of sugar in 100 c.c. of solution, or percentage by volume); usually it is referred to weight.

(*a*) SACCHAROMETER DEGREE BY WEIGHT.   This is given by various tables, the oldest, referring to 17·5°/17·5°, being Balling's, which is still used by some, although not very exact.   In commoner use is the one recalculated from Balling's data by Brix and completed by Mategczek and Scheibler; this is given below (Table VI).

For sp. gr. at 20°/4°, the concentrations are given in Table VII.

The use of these tables is indicated in the following example.

EXAMPLE : A sugar solution has the sp. gr. 1·1832 at 17·5°.   The nearest value in the table, 1·18305, corresponds with 40·7° Brix or 40·7% by weight of sugar, and interpolation shows the exact concentration to be 40·73%.

TABLE VI

Relation between Degrees Brix and the Specific Gravity at 17·5° C.

Specific gravity at 17·5° C. referred to that of water at 17·5° C.

Percentage of Sugar by Weight or Degrees Brix.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	1·00000	1·00038	1·00077	1·00116	1·00155	1·00193	1·00232	1·00271	1·00310	1·00349
1	1·00388	1·00427	1·00466	1·00505	1·00544	1·00583	1·00622	1·00662	1·00701	1·00740
2	1·00779	1·00818	1·00858	1·00897	1·00936	1·00976	1·01015	1·01055	1·01094	1·01134
3	1·01173	1·01213	1·01252	1·01292	1·01332	1·01371	1·01411	1·01451	1·01491	1·01531
4	1·01570	1·01610	1·01650	1·01690	1·01730	1·01770	1·01810	1·01850	1·01890	1·01930
5	1·01970	1·02010	1·02051	1·02091	1·02131	1·02171	1·02211	1·02252	1·02292	1·02333
6	1·02373	1·02413	1·02454	1·02494	1·02535	1·02575	1·02616	1·02657	1·02697	1·02738
7	1·02779	1·02819	1·02860	1·02901	1·02942	1·02983	1·03024	1·03064	1·03105	1·03146
8	1·03187	1·03228	1·03270	1·03311	1·03352	1·03393	1·03434	1·03475	1·03517	1·03558.
9	1·03599	1·03640	1·03682	1·03723	1·03765	1·03806	1·03848	1·03889	1·03931	1·03972
10	1·04014	1·04055	1·04097	1·04139	1·04180	1·04222	1·04264	1·04306	1·04348	1·04390
11	1·04431	1·04473	1·04515	1·04557	1·04599	1·04641	1·04683	1·04726	1·04768	1·04810
12	1·04852	1·04894	1·04937	1·04979	1·05021	1·05064	1·05106	1·05149	1·05191	1·05233.
13	1·05276	1·05318	1·05361	1·05404	1·05446	1·05489	1·05532	1·05574	1·05617	1·05660
14	1·05703	1·05746	1·05789	1·05831	1·05874	1·05917	1·05960	1·06003	1·06047	1·06090
15	1,06133	1·06176	1·06219	1·06262	1·06306	1·06349	1·06392	1·06436	1·06479	1·06522·
16	1·06566	1·06609	1·06653	1·06696	1·06740	1·06783	1·06827	1·06871	1·06914	1·C6958·
17	1·07002	1·07046	1·07090	1·07133	1·07177	1·07221	1·07265	1·07309	1·07353	1·07397·
18	1·07441	1·07485	1·07530	1·07574	1·07618	1·07662	1·07706	1·07751	1·07795	1·07839·
19	1·07884	1·07928	1·07973	1·08017	1·08062	1·08106	1·08151	1·08196	1·08240	1·C8285·
20	1·08329	1·08374	1·08419	1·08464	1·08509	1·08553	1·08599	1·08643	1·08688	1·08733·
21	1·08778	1·08824	1·08869	1·08914	1·08959	1·09004	1·09049	1·09095	1·09140	1·09185·
22	1·09231	1·09276	1·09321	1·09367	1·09412	1·09458	1·09503	1·C9549	1·09595	1·09640·
23	1·09686	1·09732	1·09777	1·09823	1·09869	1·09915	1·09961	1·I0007	1·10053	1·10099
24	1·10145	1·10191	1·10237	1·10283	1·10329	1·10375	1·10421	1·10468	1·10514	1·10560
25	1·10607	1·10653	1·10700	1·10746	1·10793	1·10839	1·10886	1·10932	1·10979	1·11026.
26	1·11072	1·11119	1·11166	1·11213	1·11259	1·11306	1·11353	1·11400	1·11447	1·11494
27	1·11541	1·11588	1·11635	1·11682	1·11729	1·11776	1·11824	1·11871	1·11918	1·11965
28	1·12013	1·12060	1·12107	1·12155	1·12202	1·12250	1·12297	1·12345	1·12393	1·12440.
29	1·12488	1·12536	1·12583	1·12631	1·12679	1·12727	1·12775	1·12823	1·12871	1·12919,

TABLE VI (continued)

Specific gravity at 17·5° C. referred to that of water at 17·5° C.

Percentage of Sugar by Weight or Degrees Brix.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
30	1·12967	1·13015	1·13063	1·13111	1·13159	1·13207	1·13255	1·13304	1·13352	1·13400
31	1·13449	1·13497	1·13545	1·13594	1·13642	1·13691	1·13740	1·13788	1·13837	1·13885
32	1·13934	1·13983	1·14032	1·14081	1·14129	1·14178	1·14227	1·14276	1·14325	1·14374
33	1·14423	1·14472	1·14521	1·14570	1·14620	1·14669	1·14718	1·14767	1·14817	1·14866
34	1·14915	1·14965	1·15014	1·15064	1·15113	1·15163	1·15213	1·15262	1·15312	1·15362
35	1·15411	1·15461	1·15511	1·15561	1·15611	1·15661	1·15710	1·15760	1·15810	1·15861
36	1·15917	1·15961	1·16011	1·16061	1·16111	1·16162	1·16212	1·16262	1·16313	1·16363
37	1·16413	1·16464	1·16514	1·16565	1·16616	1·16666	1·16717	1·16768	1·16818	1·16869
38	1·16920	1·16971	1·17022	1·17072	1·17123	1·17174	1·17225	1·17276	1·17327	1·17379
39	1·17430	1·17481	1·17532	1·17583	1·17635	1·17686	1·17737	1·17789	1·17840	1·17892
40	1·17943	1·17995	1·18046	1·18098	1·18150	1·18201	1·18253	1·18305	1·18357	1·18408
41	1·18460	1·18512	1·18564	1·18616	1·18668	1·18720	1·18772	1·18824	1·18877	1·18929
42	1·18981	1·19033	1·19086	1·19138	1·19190	1·19243	1·19295	1·19348	1·19400	1·19453
43	1·19505	1·19558	1·19611	1·19663	1·19716	1·19769	1·19822	1·19875	1·19927	1·19980
44	1·20033	1·20086	1·20139	1·20192	1·20245	1·20299	1·20352	1·20405	1·20458	1·20512
45	1·20565	1·20618	1·20672	1·20725	1·20779	1·20832	1·20886	1·20939	1·20993	1·21046
46	1·21100	1·21154	1·21208	1·21261	1·21315	1·21369	1·21423	1·21477	1·21531	1·21585
47	1·21639	1·21693	1·21747	1·21802	1·21856	1·21910	1·21964	1·22019	1·22073	1·22127
48	1·22182	1·22236	1·22291	1·22345	1·22400	1·22455	1·22509	1·22564	1·22619	1·22673
49	1·22728	1·22783	1·22838	1·22893	1·22948	1·23003	1·23058	1·23113	1·23168	1·23223
50	1·23278	1·23334	1·23389	1·23444	1·23499	1·23555	1·23610	1·23666	1·23721	1·23777
51	1·23832	1·23888	1·23943	1·23999	1·24055	1·24111	1·24166	1·24222	1·24278	1·24334
52	1·24390	1·24446	1·24502	1·24558	1·24614	1·24670	1·24726	1·24782	1·24839	1·24895
53	1·24951	1·25008	1·25064	1·25120	1·25177	1·25233	1·25290	1·25347	1·25403	1·25460
54	1·25517	1·25573	1·25630	1·25687	1·25744	1·25801	1·25857	1·25914	1·25971	1·26028
55	1·26086	1·26143	1·26200	1·26257	1·26314	1·26372	1·26429	1·26486	1·26544	1·26601
56	1·26658	1·26716	1·26773	1·26831	1·26889	1·26946	1·27004	1·27062	1·27120	1·27177

	0	1	2	3	4	5	6	7	8	9
57	1·27235	1·27293	1·27351	1·27409	1·27464	1·27525	1·27583	1·27641	1·27699	1·27758
58	1·27816	1·27874	1·27932	1·27991	1·28049	1·28107	1·28166	1·28224	1·28283	1·28342
59	1·28400	1·28459	1·28518	1·28576	1·28635	1·28694	1·28753	1·28812	1·28871	1·28930
60	1·28989	1·29048	1·29107	1·29166	1·29225	1·29284	1·29343	1·29403	1·29462	1·29521
61	1·29581	1·29640	1·297C0	1·29759	1·29819	1·29878	1·29938	1·29998	1·30057	1·30117
62	1·30177	1·30237	1·30297	1·30356	1·30416	1·30476	1·30536	1·3C596	1·30657	1·30717
63	1·30777	1·30837	1·30897	1·30958	1·31018	1·31078	1·31139	1·31199	1·31260	1·31320
64	1·31381	1·31442	1·315C2	1·31563	1·31624	1·31684	1·31745	1·31806	1·31867	1·31928
65	1·31989	1·32050	1·32111	1·32172	1·32233	1·32294	1·32355	1·32417	1·32478	1·32539
66	1·32601	1·32662	1·32724	1·32785	1·32847	1·32908	1·32970	1·33031	1·33093	1·33155
67	1·33217	1·33278	1·33340	1·33402	1·33464	1·33526	1·33588	1·33650	1·33712	1·33774
68	1·33836	1·33899	1·33961	1·34023	1·34085	1·34148	1·34210	1·34273	1·34335	1·34398
69	1·34460	1·34523	1·34585	1·34648	1·34711	1·34774	1·34836	1·34899	1·34962	1·35C25
70	1·35088	1·35151	1·35214	1·35277	1·35340	1·35403	1·35466	1·35530	1·35593	1·35656
71	1·35720	1·35783	1·35847	1·35910	1·35974	1·36037	1·36101	1·36164	1·36228	1·36292
72	1·36355	1·36419	1·36483	1·36547	1·36611	1·36675	1·36739	1·36803	1·36867	1·36931
73	1·36995	1·37059	1·37124	1·37188	1·37252	1·37317	1·37381	1·37446	1·37510	1·37575
74	1·37639	1·37704	1·37768	1·37833	1·37898	1·37962	1·38027	1·38092	1·38157	1·38222
75	1·38287	1·38352	1·38417	1·38482	1·38547	1·38612	1·38677	1·38743	1·38808	1·38873
76	1·38939	1·39004	1·39070	1·39135	1·39201	1·39266	1·39332	1·39397	1·39463	1·39529
77	1·39595	1·39660	1·39726	1·39792	1·39858	1·39924	1·39990	1·40056	1·40122	1·40188
78	1·40254	1·40321	1·40387	1·40453	1·40520	1·40586	1·40652	1·40719	1·40785	1·40852
79	1·40918	1·40985	1·41052	1·41118	1·41185	1·41252	1·41318	1·41385	1·41452	1·41519
80	1·41586	1·41653	1·41720	1·41787	1·41854	1·41921	1·41989	1·42056	1·42133	1·42190
81	1·42258	1·42325	1·42393	1·42460	1·42528	1·42595	1·42663	1·42731	1·42798	1·42866
82	1·42934	1·43002	1·43070	1·43137	1·43205	1·43273	1·43341	1·43409	1·43478	1·43546
83	1·43614	1·43682	1·43750	1·43819	1·43887	1·43955	1·44024	1·44092	1·44161	1·44229
84	1·44298	1·44367	1·44435	1·44504	1·44573	1·44641	1·44710	1·44779	1·44848	1·44917
85	1·44986	1·45055	1·45124	1·45193	1·45262	1·45331	1·45401	1·45470	1·45539	1·45609
86	1·45678	1·45748	1·45817	1·45887	1·45956	1·46026	1·46095	1·46165	1·46235	1·46304
87	1·46374	1·46444	1·46514	1·46584	1·46654	1·46724	1·46794	1·46864	1·46934	1·47004
88	1·47074	1·47145	1·47215	1·47285	1·47356	1·47426	1·47496	1·47567	1·47637	1·477c8
89	1·47778	1·47849	1·47920	1·47991	1·48061	1·48132	1·48203	1·48274	1·48345	1·48416

TABLE VII

Relation between Degrees Brix and the Specific Gravity at 20° C.

Specific gravity at 20° C., referred to that of water at 4° C.

Percentage of Sugar by Weight or Degrees Brix.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	0·998234	0·998622	0·999010	0·999398	0·999786	1·000174	1·000563	1·000952	1·001342	1·001731
1	1·002120	1·002509	1·002897	1·003286	1·003675	1·04064	1·004453	1·04844	1·005234	1·005624
2	1·006015	1·006405	1·006796	1·007188	1·007580	1·007972	1·008363	1·008755	1·009148	1·CC9541
3	1·009934	1·010327	1·010721	1·011115	1·011510	1·011904	1·012298	1·012694	1·013089	1·013485
4	1·013881	1·014277	1·014673	1·015070	1·015467	1·015864	1·016261	1·016659	1·017058	1·017456
5	1·017854	1·018253	1·018652	1·019052	1·019451	1·019851	1·020251	1·020651	1·021053	1·021454
6	1·021855	1·022257	1·022659	1·023061	1·023463	1·023867	1·024270	1·024673	1·025077	1·025481
7	1·025885	1·026289	1·026694	1·027099	1·027504	1·027910	1·028316	1·028722	1·029128	1·029535
8	1·029942	1·030349	1·030757	1·031165	1·031573	1·031982	1·032391	1·0328co	1·033209	1·033619
9	1·034029	1·034439	1·034850	1·035260	1,035671	1·036082	1·036494	1·0369c6	1·037318	1·037730
10	1·038143	1·038556	1·038970	1·039383	1·039797	1·040212	1·040626	1·041041	1·041456	1·041872
11	1·042288	1·042704	1·043121	1·043537	1·043954	1·044370	1·044788	1·045206	1·045625	1·046043
12	1·046462	1·046881	1·047300	1·047720	1·048140	1·048559	1·048980	1·049401	1·049822	1·050243
13	1·050665	1·051087	1·051510	1·051933	1·052356	1·052778	1·053202	1·053626	1·054050	1·054475
14	1·054900	1·055325	1·055751	1·056176	1·056602	1·057029	1·057455	1·057882	1·058310	1·058737
15	1·059165	1·059593	1·06c022	1·064756	1·060880	1·061208	1·061738	1·062168	1·062598	1·063029
16	1·063460	1·063892	1·064324	1·064756	1·065188	1·065621	1·066054	1·066487	1·066921	1·067355
17	1·067789	1·068223	1·068658	1·069093	1·069529	1·069964	1·070400	1·070836	1·071273	1·071710
18	1·072147	1·072585	1·073023	1·073461	1·073900	1·074338	1·74777	1·075217	1·075657	1·076097
19	1·076537	1·076978	1·077419	1·077860	1·078302	1·078744	1·79187	1·079629	1·080072	1·080515
20	1·080959	1·081403	1·081848	1·082292	1·082737	1·083182	1·83628	1·084074	1·084520	1·084967
21	1·085414	1·085861	1·086309	1·086757	1·087205	1·087652	1·88101	1·088550	1·089000	1·089450
22	1·089900	1·090351	1·090802	1·091253	1·091704	1·092155	1·092607	1·093066	1·093513	1·093966
23	1·094420	1·094874	1·095328	1·095782	1·096236	1·096691	1·097147	1·097603	1·098058	1·098514
24	1·098971	1·099428	1·099886	1·100344	1·100802	1·101259	1·101718	1·102177	1·102637	1·103097
25	1·103557	1·104017	1·104478	1·104938	1·105400	1·105862	1·106324	1·106786	1·107248	1·107711
26	1·108175	1·108639	1·109103	1·109568	1·110033	1·110497	1·110963	1·111429	1·111895	1·112361

	0	1	2	3	4	5	6	7	8	9
27	1·112828	1·113295	1·113863	1·114229	1·114697	1·115166	1·115635	1·116104	1·116572	1·117042
28	1·117512	1·117982	1·118453	1·118923	1·119395	1·119867	1·120339	1·120812	1·121284	1·121757
29	1·122231	1·122705	1·123179	1·123653	1·124128	1·124603	1·125079	1·125555	1·126030	1·126507
30	1·126984	1·127461	1·127939	1·128417	1·128896	1·129374	1·129853	1·130332	1·130812	1·131292
31	1·131773	1·132254	1·132735	1·133216	1·133698	1·134180	1·134663	1·135146	1·135628	1·136112
32	1·136596	1·137080	1·137565	1·138049	1·138534	1·139020	1·139506	1·139993	1·140479	1·140966
33	1·141453	1·141941	1·142429	1·142916	1·143405	1·143894	1·144384	1·144874	1·145363	1·145854
34	1·146345	1·146836	1·147328	1·147820	1·148313	1·148813	1·149298	1·149792	1·150280	1·150780
35	1·151275	1·151770	1·152265	1·152760	1·153256	1·153752	1·154249	1·154746	1·155242	1·155740
36	1·156238	1·156736	1·157235	1·157733	1·158233	1·158733	1·159233	1·159733	1·160233	1·160734
37	1·161236	1·161738	1·162240	1·162742	1·163245	1·163748	1·164252	1·164756	1·165259	1·165764
38	1·166269	1·166775	1·167281	1·167786	1·168293	1·168800	1·169307	1·169815	1·170322	1·170831
39	1·171340	1·171849	1·172359	1·172869	1·173379	1·173889	1·174400	1·174911	1·175423	1·175935
40	1·176447	1·176960	1·177473	1·177987	1·178501	1·179014	1·179527	1·180044	1·180560	1·181076
41	1·181592	1·182108	1·182625	1·183142	1·183660	1·184178	1·184696	1·185215	1·185734	1·186253
42	1·186773	1·187293	1·187814	1·188335	1·188856	1·189379	1·189901	1·190423	1·190946	1·191469
43	1·191993	1·192517	1·193041	1·193565	1·194090	1·194616	1·195141	1·195667	1·196193	1·196720
44	1·197247	1·197775	1·198303	1·198832	1·199360	1·199890	1·200420	1·200950	1·201480	1·202010
45	1·202540	1·203071	1·203603	1·204136	1·204668	1·205200	1·205733	1·206266	1·206801	1·207335
46	1·207870	1·208405	1·208940	1·209477	1·210013	1·210549	1·211086	1·211623	1·212162	1·212700
47	1·213238	1·213777	1·214317	1·214856	1·215395	1·215936	1·216476	1·217017	1·217559	1·218101
48	1·218643	1·219185	1·219729	1·220272	1·220815	1·221360	1·221904	1·222449	1·222995	1·223540
49	1·224086	1·224632	1·225180	1·225727	1·226274	1·226823	1·227371	1·227919	1·228469	1·229018
50	1·229567	1·230117	1·230668	1·231219	1·231770	1·232322	1·232874	1·233426	1·233979	1·234532
51	1·235085	1·235639	1·236194	1·236748	1·237303	1·237859	1·238414	1·238970	1·239527	1·240084
52	1·240641	1·241198	1·241757	1·242315	1·242873	1·243433	1·243992	1·244552	1·245113	1·245673
53	1·246234	1·246795	1·247358	1·247920	1·248482	1·249046	1·249609	1·250172	1·250737	1·251301
54	1·251866	1·252431	1·252997	1·253563	1·254129	1·254697	1·255264	1·255831	1·256400	1·256967
55	1·257535	1·258104	1·258674	1·259244	1·259815	1·260385	1·260955	1·261527	1·262099	1·262671
56	1·263243	1·263816	1·264390	1·264963	1·265537	1·266112	1·266686	1·267261	1·267837	1·268413
57	1·268989	1·269565	1·270143	1·270720	1·271299	1·271877	1·272455	1·273035	1·273614	1·274194
58	1·274774	1·275354	1·275936	1·276517	1·277098	1·277680	1·278262	1·278844	1·279428	1·280011
59	1·280595	1·281179	1·281764	1·282349	1·282935	1·283521	1·284107	1·284694	1·285281	1·285869

Table VII (continued)

Percentage of Sugar by Weight or Degrees Brix.	Specific gravity at 20° C., referred to that of water at 4° C.									
	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
60	1·286456	1·287044	1·287633	1·288222	1·288811	1·289401	1·289991	1·290581	1·291172	1·291763
61	1·292354	1·292946	1·293539	1·294131	1·294725	1·295318	1·295911	1·296506	1·297100	1·297696
62	1·298291	1·298886	1·299483	1·300079	1·300677	1·301274	1·301871	1·302470	1·303068	1·303668
63	1·304267	1·304867	1·305467	1·306068	1·306669	1·307271	1·307872	1·308475	1·309077	1·309680
64	1·310282	1·310885	1·311489	1·312093	1·312699	1·313304	1·313909	1·314515	1·315121	1·315728
65	1·316334	1·316941	1·317549	1·318157	1·318766	1·319374	1·319983	1·320593	1·321203	1·321814
66	1·322425	1·323036	1·323648	1·324259	1·324872	1·325484	1·326097	1·326711	1·327325	1·327940
67	1·328554	1·329170	1·329785	1·330401	1·331017	1·331633	1·332250	1·332868	1·333485	1·334103
68	1·334722	1·335342	1·335961	1·336581	1·337200	1·337821	1·338441	1·339063	1·339684	1·340306
69	1·340928	1·341551	1·342174	1·342798	1·343421	1·344046	1·344671	1·345296	1·345922	1·346547
70	1·347174	1·347801	1·348427	1·349055	1·349682	1·350311	1·350939	1·351568	1·352197	1·352827
71	1·353456	1·354087	1·354717	1·355349	1·355980	1·356612	1·357245	1·357877	1·358511	1·359144
72	1·359778	1·360413	1·361047	1·361682	1·362317	1·362953	1·363590	1·364226	1·364864	1·365501
73	1·366139	1·366777	1·367415	1·368054	1·368693	1·369333	1·369973	1·370613	1·371254	1·371894
74	1·372536	1·373178	1·373820	1·374463	1·375105	1·375749	1·376392	1·377036	1·377680	1·378326
75	1·378971	1·379617	1·380262	1·380909	1·381555	1·382203	1·382851	1·383499	1·384148	1·384796
76	1·385446	1·386096	1·386745	1·387396	1·388045	1·388696	1·389347	1·389999	1·390651	1·391303
77	1·391956	1·392610	1·393263	1·393917	1·394571	1·395226	1·395881	1·396536	1·397192	1·397848
78	1·398505	1·399162	1·399819	1·400477	1·401134	1·401793	1·402452	1·403111	1·403771	1·404430
79	1·405091	1·405752	1·406412	1·407074	1·407735	1·408398	1·409061	1·409723	1·410387	1·411051
80	1·411715	1·412380	1·413044	1·413709	1·414374	1·415440	1·415706	1·416373	1·417039	1·417707
81	1·418374	1·419043	1·419711	1·420380	1·421049	1·421719	1·422390	1·423059	1·423730	1·424400
82	1·425072	1·425744	1·426416	1·427089	1·427761	1·428435	1·429109	1·429782	1·430457	1·431131
83	1·431807	1·432483	1·433158	1·433835	1·434511	1·435188	1·435866	1·436543	1·437222	1·437900
84	1·438579	1·439259	1·439938	1·440619	1·441299	1·441980	1·442661	1·443342	1·444024	1·444705
85	1·445388	1·446071	1·446754	1·447438	1·448121	1·448806	1·449391	1·450175	1·450860	1·451545
86	1·452232	1·452919	1·453605	1·454292	1·454980	1·455668	1·456357	1·457045	1·457735	1·458424
87	1·459114	1·459805	1·460495	1·461186	1·461877	1·462568	1·463260	1·463953	1·464645	1·465338
88	1·466032	1·466726	1·467420	1·468115	1·468810	1·469504	1·470200	1·470896	1·471592	1·472289
89	1·472986	1·473684	1·474381	1·475080	1·475779	1·476477	1·477176	1·477876	1·478575	1·479275

TABLE VIII

Corrections of the Apparent Degree by Weight to bring it to 17·5° C.

Percentage by Weight (Degrees Brix)	0	5	10	15	20	25	30	35	40	50	60	70	75
Temperature °C.	The indication of the saccharometer is to be diminished by :												
0	0·17	0·30	0·41	0·52	0·62	0·72	0·82	0·92	0·98	1·11	1·22	1·25	1·29
5	0·23	0·30	0·37	0·44	0·52	0·59	0·65	0·72	0·75	0·80	0·88	0·91	0·94
10	0·20	0·26	0·29	0·33	0·36	0·39	0·42	0·45	0·48	0·50	0·54	0·58	0·61
11	0·18	0·23	0·26	0·28	0·31	0·34	0·36	0·39	0·41	0·43	0·47	0·50	0·53
12	0·16	0·20	0·22	0·24	0·26	0·29	0·31	0·33	0·34	0·36	0·40	0·42	0·46
13	0·14	0·18	0·19	0·21	0·22	0·24	0·26	0·27	0·28	0·29	0·33	0·35	0·39
14	0·12	0·15	0·16	0·17	0·18	0·19	0·21	0·22	0·22	0·23	0·26	0·28	0·32
15	0·09	0·11	0·12	0·14	0·14	0·15	0·16	0·17	0·16	0·17	0·19	0·21	0·25
16	0·06	0·07	0·08	0·09	0·10	0·10	0·11	0·12	0·12	0·12	0·14	0·16	0·18
17	0·02	0·02	0·03	0·03	0·03	0·04	0·04	0·04	0·04	0·04	0·05	0·05	0·06
	The indication of the saccharometer is to be increased by :												
18	0·02	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·03	0·02
19	0·06	0·08	0·08	0·09	0·09	0·10	0·10	0·10	0·10	0·10	0·10	0·08	0·06
20	0·11	0·14	0·15	0·17	0·17	0·18	0·18	0·18	0·19	0·19	0·18	0·15	0·11
21	0·16	0·20	0·22	0·24	0·24	0·25	0·25	0·25	0·26	0·26	0·25	0·22	0·18
22	0·21	0·26	0·29	0·31	0·31	0·32	0·32	0·32	0·33	0·34	0·32	0·29	0·25
23	0·27	0·32	0·35	0·37	0·38	0·39	0·39	0·39	0·40	0·42	0·39	0·36	0·33
24	0·32	0·38	0·41	0·43	0·44	0·46	0·46	0·47	0·47	0·50	0·46	0·43	0·40
25	0·37	0·44	0·47	0·49	0·51	0·53	0·54	0·55	0·55	0·58	0·54	0·51	0·48
26	0·43	0·50	0·54	0·56	0·58	0·60	0·61	0·62	0·62	0·66	0·62	0·58	0·55
27	0·49	0·57	0·61	0·63	0·65	0·68	0·68	0·69	0·70	0·74	0·70	0·65	0·62
28	0·56	0·64	0·68	0·70	0·72	0·76	0·76	0·78	0·78	0·82	0·78	0·72	0·70
29	0·63	0·71	0·75	0·78	0·79	0·84	0·84	0·86	0·86	0·90	0·86	0·80	0·78
30	0·70	0·78	0·82	0·87	0·87	0·92	0·92	0·94	0·94	0·98	0·94	0·88	0·86
35	1·10	1·17	1·22	1·24	1·30	1·32	1·33	1·35	1·36	1·39	1·34	1·27	1·25
40	1·50	1·61	1·67	1·71	1·73	1·79	1·79	1·80	1·82	1·83	1·78	1·69	1·65
50	—	2·65	2·71	2·74	2·78	2·80	2·80	2·80	2·80	2·79	2·70	2·56	2·51
60	—	3·87	3·88	3·88	3·88	3·88	3·88	3·88	3·90	3·82	3·70	3·43	3·41
70	—	5·17	5·18	5·20	5·14	5·13	5·10	5·08	5·06	4·90	4·72	4·47	4·35
80	—	—	6·62	6·59	6·54	6·46	6·38	6·30	6·20	6·06	5·82	5·50	5·33
90	—	—	8·26	8·16	8·06	7·97	7·83	7·71	7·58	7·30	6·96	6·58	6·37
100	—	—	10·01	9·87	9·72	9·56	9·39	9·21	9·03	8·64	8·22	7·76	7·42

<center>TABLE IX</center>

Correction to bring the Apparent Degree by Weight to 20° C.

Percentage by Weight	0	10	20	30	40	50	60	70	80	90
Temperature °C.	The indication of the saccharometer is to be diminished by .									
10°	0·32	0·42	0·52	0·60	0·67	0·71	0·74	0·76	0·8	0·8
11	0·30	0·39	0·47	0·54	0·61	0·65	0·67	0·68	0·7	0·7
12	0·27	0·35	0·42	0·49	0·54	0·58	0·60	0·61	0·6	0·6
13	0·25	0·32	0·38	0·43	0·48	0·51	0·53	0·53	0·5	0·5
14	0·22	0·28	0·33	0·37	0·41	0·44	0·45	0·46	0·5	0·5
15	0·20	0·24	0·28	0·32	0·35	0·37	0·38	0·38	0·4	0·4
16	0·16	0·19	0·23	0·26	0·28	0·30	0·30	0·30	0·3	0·3
17	0·12	0·15	0·17	0·19	0·21	0·22	0·23	0·23	0·2	0·2
18	0·08	0·10	0·12	0·13	0·14	0·15	0·15	0·15	0·2	0·1
19	0·04	0·05	0·06	0·06	0·07	0·08	0·08	0·08	0·1	0·1
	The indication of the saccharometer is to be increased by :									
21	0·05	0·06	0·06	0·07	0·07	0·07	0·08	0·07	0·1	0·1
22	0·10	0·11	0·12	0·14	0·14	0·15	0·16	0·15	0·2	0·1
23	0·16	0·17	0·19	0·21	0·22	0·23	0·23	0·23	0·2	0·2
24	0·21	0·23	0·26	0·28	0·29	0·30	0·31	0·31	0·3	0·3
25	0·27	0·30	0·32	0·35	0·37	0·38	0·39	0·39	0·4	0·4
26	0·33	0·36	0·39	0·42	0·45	0·46	0·47	0·47	0·5	0·4
27	0·40	0·42	0·46	0·50	0·53	0·54	0·55	0·55	0·5	0·5
28	0·46	0·49	0·54	0·57	0·61	0·62	0·64	0·63	0·6	0·6
29	0·53	0·56	0·61	0·65	0·69	0·70	0·72	0·71	0·7	0·7
30	0·60	0·63	0·68	0·73	0·77	0·79	0·80	0·79	0·8	0·8
35	0·99	1·02	1·09	1·16	1·19	1·21	1·22	1·21	1·2	1·2
40	1·41	1·46	1·54	1·60	1·63	1·64	1·65	1·63	1·6	1·6
50	2·46	2·50	2·55	2·58	2·58	2·57	2·55	2·50	2·5	2·4
60	3·68	3·73	3·72	3·67	3·61	3·57	3·50	3·41	3·3	3·2
70	5·1	5·1	5·0	4·9	4·8	4·7	4·6	4·4	4·2	4·0
80	7·1	7·0	6·8	6·6	6·3	6·1	5·9	5·6	5·3	5·0

(*b*) SACCHAROMETER DEGREE BY VOLUME.   The percentage of sugar by volume, i.e., the number of grams of sugar in 100 *true* c.c. at the temperature considered, is found by multiplying the percentage of sugar by weight by the corresponding specific gravity at the temperature considered, with reference to water at 4°.   If the sp. gr. were determined at 17·5°/17·5°, that at 17·5°/4° would be obtained by multiplying by 0·998713, which is the weight (*in vacuo*) of a *true* c.c. of water at 17·5°.   In many practical cases, especially for low percentages, this correction may be omitted without sensible error, the percentage by volume at 17·5° being obtained by multiplying the percentage by weight by the sp. gr. at 17·5°/17·5°.   When, however, the sp. gr. is determined at 20°/4°, the exact percentage by volume at 20° is obtained by multiplying the percentage by weight by the specific gravity itself.

3. Direct Determination of the Saccharometric Degree.—Instead of from tables, the percentage of saccharose may be obtained directly by special hydrometers, called *saccharometers*, which are graduated in accordance with the tables and are often used in industrial practice.   Most of these are graduated for the normal temperature 17·5° and indicate the percentage by weight, i.e., the Balling or Brix degrees (*Balling* or *Brix saccharometers*).   Now, however, there are some graduated at 20° in accordance with the decision of the Congresses mentioned above, and for particular industrial purposes at other temperatures also.   Further, saccharometers are made giving the percentages by volume.

Saccharometers usually contain in their lower part a thermometer the bulb of which constitutes, wholly or partially, the weight of the instrument.   Like hydrometers they are mostly graduated to be read at the level of the horizontal surface of the liquid, i.e., at the base of the meniscus ; some for dark liquids are an exception.

At temperatures other than the normal temperature for which they are graduated, saccharometers give *apparent degrees*, which require a correction to obtain *real degrees*.   These corrections are given in tables : for percentages by weight at 17·5° Stammer's table, based on Gerlach's data, may be used (Table VIII) ; for percentages by weight at 20°, the succeeding table (No. IX) serves ; for percentages by volume the corrections are somewhat greater.

In order to avoid the necessity of using such a table, some saccharometers are marked, beside the thermometer column, with the mean correction to be applied to the apparent degree at different temperatures.   In any case it is always advisable to use saccharometers at temperatures not far from the normal in order to obtain reliable results.

2. Refractometric Method

The *refractive index* of aqueous saccharose solutions varies with the concentration, and on this is based the determination of the sugar-content of a solution by means of the *refractometer.*

The index of refraction of saccharine liquids may be determined by the *Abbé refractometer* (*see* Essential Oils) ; the reading is made if possible at

20° and the percentage (by weight) of sugar corresponding with the index of refraction found is given by the following table (X).[1] The index of refraction read at any other temperature is corrected according to Table XI.[2]

Instead of determining the refractive index and deducing the percentage of sugar as above, a refractometer specially constructed for the sugars and giving the percentage of sugar directly may be used.[3]

TABLE X

Relation between Refractive Index and Concentration of Sugar Solutions

Refractive Index at 20°.	% of Sugar by Weight.	Refractive Index at 20°.	% of Sugar by Weight.	Refractive Index at 20°.	% of Sugar by Weight.	Refractive Index at 20°.	% of Sugar by Weight.	Refractive Index at 20°.	% of Sugar by Weight.
1·3330	0	1·3606	18	1·3920	36	1·4285	54	1·4700	72
1·3344	1	1·3622	19	1·3939	37	1·4307	55	1·4725	73
1·3359	2	1·3639	20	1·3958	38	1·4329	56	1·4750	74
1·3374	3	1·3655	21	1·3978	39	1·4351	57	1·4775	75
1·3388	4	1·3672	22	1·3997	40	1·4373	58	1·4800	76
1·3403	5	1·3689	23	1·4016	41	1·4396	59	1·4825	77
1·3418	6	1·3706	24	1·4036	42	1·4418	60	1·4850	78
1·3433	7	1·3723	25	1·4056	43	1·4441	61	1·4876	79
1·3448	8	1·3740	26	1·4076	44	1·4464	62	1·4902	80
1·3464	9	1·3758	27	1·4096	45	1·4486	63	1·4928	81
1·3479	10	1·3775	28	1·4117	46	1·4509	64	1·4954	82
1·3494	11	1·3793	29	1·4137	47	1·4532	65	1·4980	83
1·3510	12	1·3811	30	1·4158	48	1·4556	66	1·5007	84
1·3526	13	1·3829	31	1·4179	49	1·4580	67	1·5034	85
1·3541	14	1·3847	32	1·4200	50	1·4604	68	1·5061	86
1·3557	15	1·3865	33	1·4221	51	1·4628	69	1·5088	87
1·3573	16	1·3883	34	1·4242	52	1·4652	70	1·5115	88
1·3590	17	1·3902	35	1·4264	53	1·4676	71	1·5142	89
								1·5170	90

[1] As far as 65%, this table is taken from Schönrock: *Zeitschr. des Ver. der deut. Zucker-Ind.*, 1911, LXI, p. 42; the remainder is from Tolman and Smith: *Journ. Amer. Chem. Soc.*, 1906, p. 1480, and Main: *Intern. Sugar Journ.*, 1907, p. 481.

[2] This table is calculated from the data of Schönrock (*loc. cit.*).

[3] Herzfeld and Schönrock: *Zeitschr. des Ver. der deutschen Zucker-Ind.*, 1913, p. 760, and 1914, p. 10.

TABLE XI

Corrections to convert Refractive Indices at Different Temperatures to 20°

(in units in the fourth decimal place)

Percentage of Sugar by Weight	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70
Temperature °C.	The refractive index found is to be diminished by :														
10°	7	8	9	10	11	11	12	13	14	15	16	16	17	18	19
11	7	7	8	9	10	10	11	12	13	13	14	15	15	16	17
12	6	7	7	8	9	9	10	11	11	12	13	13	14	15	15
13	5	6	6	7	8	8	9	9	10	10	11	12	12	13	13
14	5	5	6	6	7	7	8	8	9	9	10	10	10	11	11
15	4	4	5	5	6	6	6	7	7	8	8	8	9	9	10
16	3	4	4	4	5	5	5	6	6	6	6	7	7	7	8
17	2	3	3	3	3	4	4	4	4	5	5	5	5	6	6
18	2	2	2	2	2	3	3	3	3	3	3	3	3	4	4
19	1	1	1	1	1	1	1	1	1	2	2	2	2	2	2
	The refractive index found is to be increased by :														
21	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2
22	2	2	2	2	2	3	3	3	3	3	3	3	4	4	4
23	3	3	3	4	4	4	4	4	5	5	5	5	5	6	6
24	4	4	4	5	5	5	6	6	6	6	7	7	7	7	8
25	5	5	6	6	6	7	7	7	8	8	8	9	9	9	10
26	6	6	7	7	8	8	8	9	9	10	10	10	11	11	12
27	7	7	8	8	9	9	10	10	11	11	12	12	13	13	14
28	8	9	9	10	10	11	11	12	12	13	13	14	15	15	16
29	9	10	11	11	12	12	13	13	14	15	15	16	16	17	18
30	10	11	12	12	13	14	14	15	16	16	17	18	18	19	20
31	12	12	13	14	15	15	16	17	17	18	19	19	20	21	22
32	13	14	14	15	16	17	18	18	19	20	21	21	22	23	24
33	14	15	16	17	18	18	19	20	21	21	22	23	24	25	26
34	16	16	17	18	19	20	21	22	22	23	24	25	26	27	28
35	17	18	19	20	21	21	22	23	24	25	26	27	28	29	30
36	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32

3. Polarimetric Method

1. Rotatory Power.—This name designates the property possessed by many organic substances (optically active compounds), including sugars, of rotating the plane of polarised light passing through liquids containing them. The rotations may be to the left or to the right, the substances causing them being *lævo-* or *dextro-rotatory*.

For any liquid, the extent of the rotation is proportional to the thickness of the layer traversed by the light. Further, the angle for one and the same substance depends on:

1. The concentration of the solution. In some cases angle and concentration are proportional, but in others there is more or less divergence.

2. The temperature. This has a small influence with some substances, and a large one with others, and the change may be in either direction. Rotations are usually referred to 20° C.

3. The wave-length of the light used. The rotation is greater for the short violet rays than for the longer red ones. Monochromatic light, mostly yellow sodium light, corresponding with Fraunhofer's D line, is generally employed.

4. The nature of the solvent. Other conditions being equal, the rotation sometimes changes with the solvent.

5. Some active substances exhibit different rotations according as the solution is freshly prepared or otherwise, a constant value being attained only after the lapse of some time. This phenomenon is termed *mutarotation*.

To express the rotations produced by different substances under comparable conditions, the *specific rotation* is calculated. This represents the rotation which would be produced by a liquid containing 1 gram of active substance per c.c. when a ray of polarised light traverses a layer of it 1 decimetre in length. The specific rotation is denoted by the symbol $[\alpha]$ or, when it refers to yellow sodium light and to the temperature 20° C., by $[\alpha]_D^{20}$.

For active liquids, the specific rotation is given by the formula:

$$[\alpha] = \frac{a}{l\,d},$$

where a = observed angle of rotation, either dextro ($+$) or lævo ($-$), in degrees and decimals of a degree;

l = length of the liquid traversed in decimetres;

d = specific gravity of the liquid at the temperature of the experiment, referred to water at 4° C.

For active substances examined in solution (in an inactive solvent) the specific rotation is given by the formula:

$$[\alpha] = \frac{100\,a}{l\,c},$$

where c indicates the concentration, i.e., the number of grams of active substance in 100 c.c.[1] of solution measured at the experimental temperature.

---

[1] True c.c., i.e., equal to the volume occupied by 100 grams of water at 4° weighed in a vacuum.

If p is the percentage of active substance by weight in the solution, and d the specific gravity of the latter at the temperature of observation (referred to water at 4° C.), $c = p\,d$, so that the preceding formula becomes :

$$[a] = \frac{100\ \alpha}{l\,p\,d}.$$

It should be noted, however, that in cases where the rotation varies with the concentration, these two formulæ give the specific rotation only for the actual concentration used.

2. Polarimeters.—The apparatus used for the determination of the rotation of the plane of polarisation is termed a *polarimeter*.

In its simplest form, the polarimeter consists of two prisms of Iceland spar cut through and reunited in a definite way ; the best known and simplest of these is the *Nicol's prism* or, shortly, *nicol*.[1] One of the prisms, behind which a source of light is placed, is fixed and has the function of polarising the light passing through it, and is thus termed the *polariser*. The other, in front of which is the observer's eye, is rotatable on its axis and is furnished with an index moving over a graduated circle ; this is named the *analyser*, as it permits of the determination of the rotation which the polarised light has undergone. When the planes of polarisation of the two prisms are parallel, the analyser allows the polarised rays to pass, but when the analyser is rotated, it no longer permits of the complete passage of the rays and the light reaching the eye is weakened. The extent of the weakening increases as the analyser is turned until no light passes when the analyser occupies a position at right angles to its original one ; when this is the case the index should be at the zero of the graduated circle.

If an optically active substance is now interposed between the two prisms, the plane of polarisation is deviated by a certain angle and the field becomes more or less highly illuminated ; it is rendered dark again by rotation of the analyser, the extent of this rotation being read off on the graduated circle.

In practice, observations are made easier and more exact by the introduction into the polariser of arrangements and devices such that the field visible through the eye-piece is divided into two or more zones, these being equally illuminated only for a definite position of the analyser. This position is easy to fix exactly, since the line of separation of the zones is then scarcely visible, whereas a slight displacement causes the immediate appearance of the contrast between the differently illuminated zones. Such position is taken as the standard, and since in it there is neither darkness nor a maximum of light, the apparatus is known as a *half-shadow polarimeter*.

One of the commonest of these is that of Laurent, shown in Fig. 40 and, as regards its essential optical parts, in Fig. 39.

The *Laurent polarimeter* consists of a foot supporting a horizontal metallic

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[1] This is a prism of Iceland spar, about three times as long as thick, with an angle of 68°, cut diagonally so as to divide it into two right-angled triangular prisms, which are then reunited with Canada balsam. When a ray of light penetrates the prism, of the two refracted rays, the ordinary undergoes total reflection at the layer of balsam, whilst the extraordinary passes through the prism polarised.

tube the middle part of which is fashioned like a semi-cylindrical channel with a hinged cover ; inside this the tube containing the liquid to be examined is placed.   This channel carries at one end the polarising apparatus and at the other the analyser.   The polarising apparatus consists of a lens L (*see* Fig. 39), which collects the rays from a sodium flame [1] ; of a polarising nicol P ; of a thin quartz plate Q cut parallel to the optical axis of the crystal and fixed to a circular diaphragm so as to occupy exactly one-half of the aperture.   The analysing apparatus consists of an analysing nicol A and a tubular eye-piece O ; by means of a milled head it is rotatable
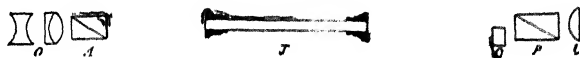
FIG. 39
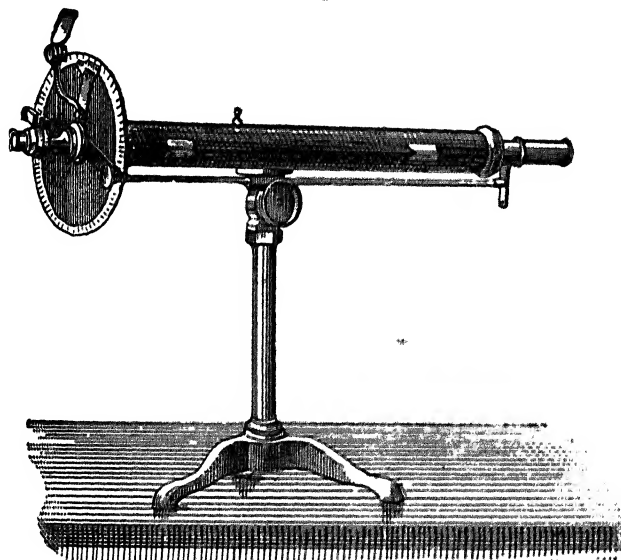
FIG. 40

on its axis, together with a vernier which passes round a graduated circle and may be observed with a lens.

The thickness of the plate Q is such that when the vernier is at zero the right and left halves of the field in the eye-piece appear equally intensely illuminated.   Before, however, the instrument is used, it must be ascertained that the two halves are really equally bright when the vernier is at zero ; if this is not the case, there is a displacement of the zero, which may be corrected by means of a regulating screw.   When this has been done, the tube T of exactly determined length closed at the ends with two glass plates and containing the solution to be examined, is interposed.[2]   If the liquid

[1] This is obtained by a simple or double bunsen burner fitted at a certain height with a chimney ; in the hottest part of the flame is placed a platinum gauze spoon containing sodium chloride (or better a calcined mixture of 380 parts of crystallised trisodium phosphate and 59 parts of sodium chloride).   To obtain an absolutely monochromatic light, the light should be passed through a plate or solution of potassium dichromate, which in the Laurent polarimeter may be inserted between L and P (Fig. 39).

[2] For the construction of the tubes and precautions to be taken in using them, *see* later under Saccharimeters.

is not optically active, the field still appears uniform ; if, however, the liquid is dextro- or lævo-rotatory the right-hand half will be darker or paler than the other. The analyser is then rotated so that the vernier is moved towards the right or left until the field is again uniform. The angle of deviation, a, is then read off and the specific rotation calculated.

3. Saccharimeters.—For saccharine solutions use is made of polarimeters with a special graduation, these being termed saccharimeters.

Two principal methods of graduation are in use in saccharimeters. In the *Soleil scale*, the rotation of the plane of polarisation given by a quartz plate 1 mm. thick is taken as 100. In the *Ventzke scale*, which is the more commonly employed, the rotation due to a pure saccharose solution of specific gravity 1·1 at 17·5° C. and 20 cm. in length is taken as 100.

(*a*) NORMAL WEIGHT. The weight of saccharose which must be present in 100 c.c. of solution in order that a length of 20 cm. of the liquid may give a rotation of 100 on the saccharimeter is termed the *normal weight*.

For the Soleil scale the normal weight has been determined at different times by various authors with somewhat divergent results (16·02–16·47) ; the most probable value and that actually adopted in France is 16·29 grams.[1]

As regards the Ventzke scale, it was first established that the weight of saccharose to be dissolved in 100 c.c. (so-called Mohr c.c.) to obtain a solution of specific gravity 1·1 at 17·5° C. is 26·048 grams, and this was taken as the normal weight for these saccharimeters. Each division on this scale will therefore correspond with 0·26048 gram of saccharose per 100 cc. and a solution containing the normal weight per 100 c.c. of a product containing saccharose (and no other optically active substance) will give a reading on the scale which is the actual percentage of saccharose in the substance.

The *Mohr c.c.* represents the volume occupied at 17·5° C. by 1 gram of water, weighed in air with brass weights ; 100 Mohr c.c. equal 100·235 true c.c., so that 100 true c.c. at 17·5° C. of normal saccharose solution will contain 25·987 grams. The measuring flasks used in sugar analysis when the above normal weight (26·048 grams) is adopted are gauged according to Mohr, and the distilled water required to fill them to the mark at 17·5° C. should weigh exactly the number of grams marked on the flask.

It should, however, be mentioned that the International Commission for Standard Methods of Sugar Analysis, as a result of the deliberations of the International Congress of Applied Chemistry, decided at their Paris meeting in 1900 to make use of the *true c.c.* (the volume occupied at 4° C. by 1 gram of water weighed in a vacuum) instead of the Mohr c.c. ; it is also decided that the volume should be measured at 20° C., at which temperature the polarimetric readings are to be made. Under these conditions the normal weight to be employed is 26 grams,[2] i.e., the rotation 100 with saccharimeters with the Ventzke scale is obtained by dissolving 26·000 grams of pure saccharose, weighed in air with brass weights (equal to 26·016 grams

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[1] *Sucrerie indigène*, 1900, LVI, p. 295. *See also* Nasini and Villavecchia : Normal Weight for Saccharimeters, *Ann. Labor. Chim. Centr. Gabelle*, 1893, II, p. 47.

[2] In recent years the adoption of a single saccharimetric scale with the normal weight 20 grams has been suggested, but it is not yet in use.

weighed in a vacuum), in 100 true c.c. (equal to the volume of 100 grams of water at 4° weighed in a vacuum) at 20° C. and reading at 20° C. in a tube 20 cm. long. For testing flasks graduated in accordance with this new definition, it should be remembered that 100 true c.c. of water at 20° weigh 99·7174 grams, weighed in air with brass weights (equal to 99·8234 grams weighed in a vacuum). This will then represent the weight of water required to fill the 100 c.c. (true) flask at 20° C.[1]

A variation of a few milligrams in the case of 100 c.c. flasks is allowable, the ordinary variations in the density of the air being sufficient to introduce a difference in the third decimal figure. For ordinary purposes, flasks with an error not greater than ± 0·05 per 100 c.c. may be used.

(b) DESCRIPTION OF THE APPARATUS. Any half-shadow polarimeter, suitably graduated, may be used as a saccharimeter. For instance, the Laurent polarimeter is often provided, on its graduated circle, with the saccharimetric scale (usually that of Soleil, the 100 point corresponding with 21° 14') as well as the ordinary degree scale.

Those saccharimeters with a Ventzke scale which are commonly used (also half-shadow) are, however, constructed according to another system, that of *compensation*, of which there are two principal types : *simple* and *double compensation*. The arrangement of the essential optical parts of these two forms of saccharimeter will first be indicated, and the construction of the latest and most perfect model will then be described in detail.

In the *saccharimeter with simple compensation*, the optical parts of which are shown diagrammatically in Fig. 41, the light rays traverse first a system

FIG. 41

of convergent lenses L and are thus concentrated on the half-shadow polariser P (constructed according to Jellet and Cornu's principle or according to that of Lippich), which divides the field of vision into two zones separated by a vertical straight line. The rays, which are thus polarised, pass through the tube T containing the solution to be examined, then through a quartz plate with parallel faces H and two wedge-shaped quartz plates M and N with rotation of the opposite sign to that of H. Of these two plates, which constitute the *compensator*, one, N, is stationary, whilst the other, M, can move parallel to its original position so as to alter only the total thickness of quartz in the compensator. Beyond the compensator comes the polarising nicol A, and lastly an eye-piece tube O. When the tube T is not in the apparatus and the movable wedge M is in such a position that the total thickness of the two wedges is equal to that of the plate H, the two halves of the field of the eye-piece are equally illuminated ; in such position the zero of the scale (marked on the framework of the movable wedge) coincides with the zero of the vernier (marked on the framework of the stationary wedge). If, however, the tube T containing the sugar solution is inter-

[1] See *Zeitschr. des Ver. der deutsch. Zucker-Ind.*, 1900 (general part), p. 357.

posed, the two halves of the eye-piece field appear unequally illuminated, and to restore uniformity the movable wedge must be displaced until the difference in thickness between the plate H and the wedge-system M–N counterbalances the rotation of the solution. The scale is so graduated that a solution containing the normal weight of pure saccharose in 100 c.c., observed under the prescribed conditions, gives uniformity of the field when the zero of the vernier coincides with 100 on the scale.

In *saccharimeters with double compensation* (Fig. 42), the place of the parallel-faced quartz plate H is taken by a second pair of wedges, one (K) stationary and the other (H) movable, having rotations of opposite sign to M and N (and carrying also another vernier and the corresponding scale) ; the other optical parts correspond with those of saccharimeters with simple compensation. When the zeros of the two scales coincide with those of
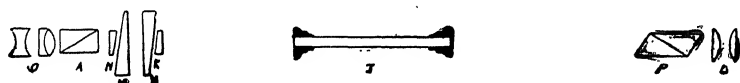
FIG. 42

the respective verniers, the field is evenly illuminated. If, then, the normal saccharose solution is interposed and one of the movable wedges carrying what is termed the *working scale* is moved whilst the other—with the *control scale*—remains at zero, uniformity of field is again attained when the working scale indicates 100. If now the solution is removed and the control scale moved, uniformity reappears when the control scale indicates the same number as the working scale.

A saccharimeter of the latest model is shown in Fig. 44 and its optical parts in Fig. 43. It will be seen that it is a double compensation instrument and differs from the preceding only as regards the polariser. The latter, made on Lippich's principle, consists of a system of three prisms and causes the field to be divided into three parts by two vertical lines ; when the field is not uniformly illuminated, the two outer zones are illuminated equally, but differently from the middle one.

The instrument is carried on a heavy two-footed base, which gives it great stability, and consists of a horizontal tube with its middle portion, as in all polarimeters, in the form of a semi-cylindrical channel provided with a hinged cover and made to hold the tube with the sugar solution. At one end of the instrument is the polariser and at the other the analyser, which is completely enclosed in a metal case so that the wedges and scales are preserved from dust and from external agents, this being highly advantageous. The movable wedges are displaced by means of two long screws shown at the bottom left-hand corner of Fig. 44 (the lower screw operates the working scale and the upper one the control scale). The scales and their verniers, which are marked on the upper part of the metal casing of the wedges, are reflected into the field of a separate eye-piece shown at the left of the figure.

The apparatus should be tested before use. The zero is first verified and if, when one scale reads 0 and the field is uniformly illuminated, the other scale does not read 0 also, one of the fixed wedges must be carefully

moved by means of a suitable key.   The 100 point and other points on the scale may be verified by means either of solutions of pure saccharose of definite strength,[1] or of quartz plates of known exact rotations, care being taken to observe all the precautions indicated below.

(*c*) LAMP.   Unlike those of the Laurent type, compensation sacchari-meters do not require yellow light, but are used with a constant, bright white light.   The older lamps, burning gas or petroleum, consisted of several fan-shaped flames placed one behind the other and enclosed in a blackened metal cylinder, which allowed the light to pass out only through a circular aperture.   The latter was usually provided with a so-called con-densing lens, but it is now recognised that this merely hindered the passage
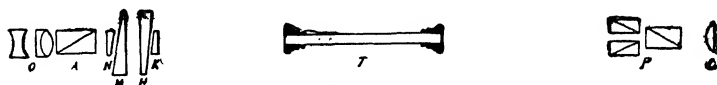
FIG. 43
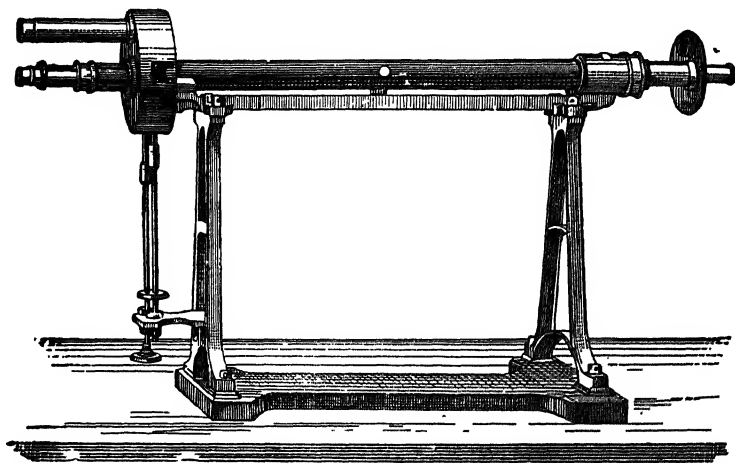
FIG. 44

of the rays into the apparatus.   The newest lamps are gas (or spirit) lamps furnished with an incandescent mantle and arranged in a blackened metallic cylinder with a ground-glass aperture in the front part.   An incandescent electric lamp (32–50 candles) with a ground-glass bulb and arranged in a metal cylinder is also used ; this gives out little heat and is thus of great advantage, since the temperature of the instrument and its surroundings is not changed much—a point of special importance when many successive readings are to be made.[2]

The source of light must lie in the direction of the axis of the instru-

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[1] The saccharose used should be crystallised several times from water, then pre-cipitated from the aqueous solution by means of alcohol, and finally dried at 60–70° to constant weight.   It should not contain moisture or ash in sensible amount and should not react with Soldaini's liquid (*see* Chemical Methods, p. 108, note [4]).

[2] Electric lamps are also made which are fixed firmly to the polarimeter itself.

ment so as to illuminate uniformly the field of view, the distance being arranged so that the readings are as sharp as possible ; it should not be displaced during the observations.[1]

In some cases, especially with almost colourless liquids, the zones of the field of vision exhibit somewhat different colours, which prevents accurate readings being obtained.   This inconvenience is avoided by introducing a suitable plate of potassium bichromate into the eye-piece or by interposing between the lamp and the saccharimeter a glass cell with parallel faces (Landolt's so-called ray-filter) containing an aqueous solution of this salt [2] ; by this means the more refractive rays are absorbed and the field assumes a uniform yellow tint.

(d) SACCHARIMETER TUBES.   These are usually of glass and 20 cm. long, but longer ones (30, 40, 50 and 60 cm.) are used for liquids of low rotation and shorter ones (10, 5, 2·5 cm.) for highly coloured liquids.   They are closed at the ends by glass discs kept in position by screw caps (or spring or simple friction caps) fitted inside with a rubber ring.   The length of the tube must be very exact and this is checked by means of apparatus based, like the dividing engine, on the use of a micrometer screw.[3]   The ends of the tube should be exactly perpendicular to the axis, and the end glasses should have perfectly plane and parallel faces and should be made of clear, absolutely optically inactive glass.   The tubes are filled immediately before reading and are carefully cleaned immediately afterwards.

To fill a tube this must be cleaned and well dried, closed at one end and held vertically with the open end up, the solution being then poured in until it fills the tube and arches over the top.   The glass disc is then placed on the tube so as to expel the excess of liquid, which is absorbed with a strip of filter paper.   The screw cap is then placed in position and screwed down until it just holds.

When it is necessary to control the temperature of the liquid, the tube is opened at one end immediately after the reading and a thermometer inserted.   Better still, in cases where variations of temperature exert a marked influence on the result, special tubes may be used which are furnished with a T-branch containing a stopper traversed by a thermometer and are surrounded by a metallic jacket through which water at constant temperature is circulated.

For the successive and rapid reading of different liquids often required in sugar factories, so-called continuous polarisation tubes have been devised, these being furnished with a tube at each end ; suction at one of these, which is connected with a rubber tube bent to form a siphon, results in

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[1] To be more exact, the distance from the lamp to the instrument should be such that the image of the point of a wire placed immediately before the source of light is formed sharply on a sheet of white paper supported at the diaphragm of the analyser ; in any event, however, such distance should not be less than 15 cm. in order that the heat of the lamp may neither damage the optical parts of the apparatus nor alter the experimental results.

[2] To obtain readings saccharimetrically comparable, the bichromate solution (concentration 6% and thickness 1·5 cm.) should always be interposed.

[3] For tubes in ordinary use, the length of that of 20 cm. should not differ more than 0·1 mm. from the truth ; otherwise a correction should be applied to the readings.

entry of the liquid at the other. When the reading is made, the liquid is expelled and another introduced and so on.

(e) METHOD OF READING. Polarimetric readings should be made in a dark room, if possible with black walls.

When the lamp is arranged in its place, the field of the apparatus is observed through the eye-piece, care being taken that the observer's position is a comfortable and natural one for looking along the axis of the apparatus ; the eye should be 1–3 cm. from the eye-piece. The latter is focussed so that the separation between the vertical zones of the field is seen as a thin, straight line. The field should be perfectly circular and well illuminated throughout ; if this is not the case, the lamp is moved.

The reading is then made and, in order to detect small non-uniformities in the field, it is advisable to rest the eye for about half a minute between one reading and the next.

With saccharimeters provided with the Ventzke scale, the latter extends from 0 to 100 in the positive direction and from 0 to,— 30 in the negative direction ; the vernier is divided into ten parts, the total length corresponding with nine scale divisions. When the zero of the vernier does not coincide exactly with a division on the scale, the figure after the decimal point is given by that division of the vernier which does coincide with a scale division counting from either the zero or the 10 point of the vernier according as the reading is positive or negative. If the scales are sufficiently clear and highly magnified, 0·05 of a division can be estimated.

EXAMPLES : Figures 45, 46 and 47 represent respectively the readings + 25·3, − 4·6 and + 8·25.
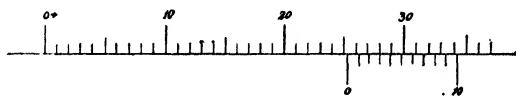
FIG. 45
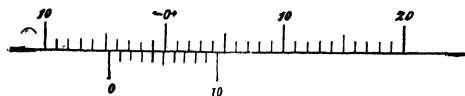
FIG. 46
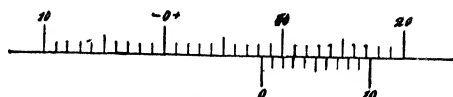
FIG. 47

The method of making the reading varies according as the instrument is one with simple or double compensation.

(a) Simple compensation : (1) The screw of the scale is turned until the field appears uniformly illuminated and by small movements in both senses the exact point is attained at which the separation between the zones of the field is seen either not at all or as little as possible. The scale

should then read zero if the instrument is perfectly adjusted.   If, however, there is a deviation and it is not desired to eliminate it by adjustment of the apparatus, the reading is taken by means of the vernier, the sign being noted.

(2) The tube containing the sugar solution is introduced and the screw again turned until the field once more appears evenly illuminated.   The scale is again read and the reading increased or diminished by the zero error according as this is of the opposite or of the same sign as the reading.

(b) Double compensation :

(1) The tube with the sugar solution is placed in the saccharimeter ; the control scale is placed exactly at zero and the lower screw, corresponding with the working scale, turned until the field appears uniform ; the working scale is then read.

(2) The tube is removed, the field brought back to uniformity by means of the control screw and this scale read ; the reading should be equal or nearly equal to the preceding reading.

(3) The tube is then replaced in the saccharimeter, the field brought back to uniformity by moving the screw of the control scale, and the latter read ; this reading will be equal or nearly equal to zero.

(4) The tube is then taken out, the field brought again to uniformity by means of the working scale and this read, the reading being zero or nearly zero.

When the four readings are made, the result is calculated by taking the mean of the first two and the mean of the second two (taking account of the sign) and adding or subtracting the two means according as they are of contrary or the same sign.   This calculation will be clear from the following examples :

$$
A\begin{cases} \text{Readings :} \begin{cases} (1) & + 89 \cdot 3 \\ (2) & + 89 \cdot 5 \end{cases} \quad \begin{matrix} (3) & + 0 \cdot 1 \\ (4) & - 0 \cdot 2 \end{matrix} \\ \text{Means :} \qquad + 89 \cdot 4 \qquad\qquad - 0 \cdot 05 \\ \text{Result :} \qquad\qquad + 89 \cdot 45 \end{cases}
$$

$$
B\begin{cases} \text{Readings :} \begin{cases} (1) & + 45 \cdot 15 \\ (2) & + 45 \cdot 25 \end{cases} \quad \begin{matrix} (3) & + 0 \cdot 05 \\ (4) & + 0 \cdot 15 \end{matrix} \\ \text{Means :} \qquad + 45 \cdot 20 \qquad\qquad + 0 \cdot 10 \\ \text{Result :} \qquad\qquad + 45 \cdot 10 \end{cases}
$$

$$
C\begin{cases} \text{Readings :} \begin{cases} (1) & - 7 \cdot 10 \\ (2) & - 7 \cdot 15 \end{cases} \quad \begin{matrix} (3) & 0 \\ (4) & - 0 \cdot 05 \end{matrix} \\ \text{Means :} \qquad - 7 \cdot 13 \qquad\qquad - 0 \cdot 03 \\ \text{Result :} \qquad\qquad - 7 \cdot 10 \end{cases}
$$

4. Polarimetric Constants of the Principal Sugars.—Table XVI (*see* later) contains the polarimetric constants of the sugars more commonly met with in the analysis of commercial products ; a brief statement of these data may be given here.

(*a*) POLARIMETRIC CONSTANTS IN CIRCULAR DEGREES.   The specific rotations of the different sugars and their variation with temperature and concentration have been determined by various authors.   In the table mentioned, the first column gives the value of $[a]_D^{20}$ regarded as most reliable ;

when the rotation varies sensibly with the concentration, the value given must be taken to be the mean value for medium concentrations (10–15%). The variations with concentration and temperature will now be considered.

For *saccharose*, the value + 66·5° may be regarded as almost constant for concentrations at least up to the normal (26 grams in 100 c.c.) and is deduced from the formula [1] :

$$[a]_D^{20} = 66·438 + 0·01032\ p - 0·00035449\ p^2,$$

where p is the percentage of saccharose by weight in the solution ; this formula holds for values of p between 3 and 65. The variation with the temperature is also not very marked ; for concentrations near to the normal and for temperatures between 10° and 32°, Schönrock's data [2] show that the specific rotation of saccharose diminishes by 0·0144° for each 1° rise in temperature.

For *invert sugar*, the variation of the specific rotation with the concentration is marked and is expressed by the formula [3] :

$$[a]_{D_1}^{20} = -19·447 - 0·06068\ p + 0·000221\ p^2,$$

where p, the percentage by weight of the sugar in the solution, lies between 9 and 68 ; or by

$$[a]_D^{20} = -19·657 - 0·03611\ c,$$

where c, the weight of invert sugar in 100 c.c., is not greater than 35. The value '— 20·2° of the table is deduced from this formula for concentrations up to 15%.

The variation with the temperature is given by the following formula, which holds between 0° and 30° and shows that at temperatures in the neighbourhood of 20°, a diminution occurs in the rotatory power of about 0·31° for 1° increase in temperature :

$$[a]_D^t = [a]_D^{20} + 0·30406\ (t - 20) + 0·001654\ (t - 20)^2.$$

For *glucose*, the influence of temperature is negligible. The value 52·8°, given in the table, may be regarded as sufficiently exact for the concentrations 10–15% and is derived from the formula [4] :

$$[a]_D = 52·50 + 0·018796\ p + 0·0051683\ p^2,$$

where p is the percentage by weight of glucose (anhydrous) in the solution.

For *levulose* or *fructose*, the variations of specific rotation with temperature and concentration are considerable, but the data are somewhat discordant and uncertain, owing to the difficulty of obtaining this sugar pure and crystalline. The value — 93° given in the table, which is in satisfactory agreement with those adopted for glucose and invert sugar, is deduced for about 10% solutions from the formula [5] :

$$[a]_D^{20} = -(91·90 + 0·111\ p) ;$$

[1] Nasini and Villavecchia : Normal Weight for Saccharimeters, *Ann. Labor. chim. Centr. Gabelle*, 1893, Vol. II, p. 47.
[2] *Zeitschr. des Ver. der deutschen Zucker-Ind.*, 1900, L, pp. 413–434.
[3] Gabbe : *Zeitschr. des Ver. für Rübenzuckerind.*, 1884, XXXIV, p. 1345.
[4] Tollens : *Ber. deut. chem. Gesell.*, 1884, XVII, p. 2238.
[5] Ost : *ibid.* 1891, XXIV, p. 1636.

where p, the percentage by weight of levulose in the solution, lies between 3 and 30. For medium concentrations, a rise of temperature of $1°$ is accompanied by diminution in the specific rotation by $0.67°$.

With *maltose* (anhydrous):

$$[\alpha]_{D}^{t} = 140.375 - 0.01837\ p - 0.095\ t,$$

so that for ordinary concentrations at $20°$ C. the value is $+ 138.2°$.[1]

With *lactose*, variation with concentration is negligible; $[\alpha]_{D}^{20} = + 52.53°$ for the hydrated sugar, $C_{12}H_{22}O_{11} + H_2O$.[2] This number diminishes by $0.075°$ for $1°$ rise of temperature.

With *raffinose*, the variation with concentration or temperature is very slight, the value for the hydrate $(+ 5H_2O)$[3] being $+ 104.5°$. This value is 1.5715 times that for saccharose, while the value for anhydrous raffinose is 1.1786 times that for hydrated raffinose and 1.852 times that for saccharose.

From the mean specific rotations, calculations have been made, for each sugar, of the other data relating to polarimetric readings in circular degrees (*see* Table XVI). For those sugars with which the rotatory power varies appreciably with concentration and temperature, these data are, of course, exact only at $20°$ and for the usual concentrations.

(*b*) SACCHARIMETRIC CONSTANTS. Table XVI contains also the corresponding constants relating to the Ventzke scale; those for *saccharose* are deduced from the normal weight (26 or 26.048 grams: *see* above) and may be regarded as valid for any concentration.[4] The influence of temperature on the readings of saccharose solutions in the saccharimeter may usually be disregarded, but the temperature should not differ much from $20°$ or, at any rate, the reading should be made at the temperature at which the solution is prepared. If, however, the solution is made at $20°$ and the reading at $t°$ (this being the temperature of the quartz of the compensator), the saccharimetric reading of a normal solution should be increased by $0.061\ (t - 20)$.[5]

As regards *invert sugar*, a normal solution of saccharose contains, after inversion, 27.419 (or 27.369) grams of invert sugar, if the normal weight is taken as 26.048 (or 26) grams; such an inverted solution, made up to the doubled volume and read in a 20 cm. tube, gives a reading of $- 16.33$ divisions at $20°$. If there were no change of volume, the resulting solution would have the rotation $- 32.66$ divisions (disregarding variation of the specific rotation with the concentration). The variation per $1°$ of temperature is 0.5 of a division, so that the rotation of the solution at temperature $t°$ may be expressed by $- 42.66 + 0.5\ t$, $- 42.66$ being the reading at $0°$ C.

[1] Meissl: *Journ. für prakt. Chemie*, Series 2, Vol. XXV, p. 114.

[2] Schmöger: *Ber. deut. chem. Gesell.*, 1880, XIII, p. 1922; Parcus and Tollens: *Liebig's Annalen der Chemie*, Vol. 257, p. 170; Denigès and Bonnans: *Journ. de pharm. et chim.*, Series 5, Vol. 17, p. 363.

[3] Tollens: *Liebig's Annalen der Chemie*, Vol. 232, p. 169.

[4] For saccharose, 1 Ventzke division (using Mohr c.c.) corresponds with 0.3465 circular degrees; this ratio varies somewhat for different substances according as the dispersive power varies, but in general is almost constant for the different sugars.

[5] *Zeitschr. des Ver. der deutschen Zucker-Ind.*, 1901, LI, p. 106; 1903, LIII, p. 650.

The constants given in Table XVI refer only to medium concentrations.[1]

For *glucose*, the normal weight is 32·81 grams (or 32·75 grams) when the volume is measured in Mohr c.c. (or in true c.c. at 20°).

For *levulose*, the constants given are calculated from those of glucose and of invert sugar; the marked variation of the rotation with the temperature and concentration renders polarimetric observations of this sugar somewhat inexact.

For *maltose*, *lactose* (hydrated) and *raffinose* (hydrated), the normal weights are respectively 12·55 (or 12·58) grams, 32·88 (or 32·95) grams,[2] and 16·545 (or 16·576) grams, according as the volume is measured in true (or Mohr) c.c.

In polarimetric determinations, the mutarotation must always be taken into account, this being greatest in glucose and less marked in levulose, invert sugar, maltose and lactose. Solutions of these sugars do not assume constant rotations until they have been prepared about 24 hours or kept at a high temperature for a short time.

4. Chemical Method

1. Fehling's Solution.—The chemical method for the determination of sugars is based on the reducing power they exert on an alkaline solution of copper, this power being exhibited in varying degree by all the sugars dealt with here excepting saccharose and raffinose. The reduction is manifested by the formation of a red precipitate of cuprous oxide. The cupric solution usually employed is *Fehling's solution*, obtained by mixing equal volumes of the two following solutions just before using:

(1) 69·278 grams of pure crystallised copper sulphate ($CuSO_4 + 5H_2O$) are dissolved in water to 1 litre.[3]

The copper sulphate to be used is purified by repeated crystallisation from water, the solution being kept shaken during crystallisation; it is then dried in the air between filter papers.

(2) 346 grams of Rochelle salt and 100 grams of sodium hydroxide are dissolved in water to 1 litre.

The two solutions are stored separately in bottles closed by rubber stoppers through which pass the pipettes used to withdraw the solutions.[4]

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[1] *See also* note 1 on p. 116.

[2] According to more reliable results, the normal weight of lactose is 32·91 (or 32·97) grams for true (or Mohr) c.c.

[3] The concentration of the copper solution was based originally on the assumption that 1 mol. of glucose (or invert sugar or levulose) reduced 5 mols. of copper sulphate —which is only approximately true—and it was calculated (with the old atomic weights) so that 100 c.c. of the copper solution, with the corresponding quantity of the alkaline solution, would be reduced by 1 gram of such sugars. The concentration given above is that commonly used, although some authors have suggested slight modifications.

[4] Fehling's solution is also reduced, although only to a minimal extent, by saccharose, so that, in the qualitative investigation of small quantities of reducing sugars, it is well to replace it by *Soldaini's solution*. This is prepared by dissolving 150 grams of potassium bicarbonate and 101·4 grams of normal potassium carbonate in water, adding 100 c.c. of the copper sulphate solution used for Fehling's solution and making the volume up to a litre.

The determination of the reducing sugars may be either volumetric or gravimetric.

2. Gravimetric Determination of Sugars with Fehling's Solution.—As a rule the cuprous oxide obtained by boiling the sugar solution with Fehling's solution is reduced to metallic copper, which is weighed. It is, however, necessary to follow exactly the procedure prescribed for each particular method, especially as regards the dilution and volume of the solutions, the duration of the boiling and the mode of filtration.

The general procedure for all cases is as follows :

1. GENERAL PROCEDURE. Equal volumes of the two constituents of Fehling's solution and the proper amount of water are heated in a 250–300 c.c. conical flask over an aperature 6·5 cm. in diameter in an asbestos card, the latter being supported on a wire gauze.

In some cases the sugar solution is added at the beginning, and in others only when the liquid begins to boil, the boiling being maintained for a definite time. At the end of this time, the flame is removed and about 100 c.c. of water, previously boiled and cooled, immediately added to the solution. The latter is at once filtered through a filter-tube containing asbestos (described in detail below) with the aid of a water-pump, the tube being kept filled with liquid. The precipitated cuprous oxide is then washed 12–15 times with hot, boiled water, 300–400 c.c. in all being used. The filter is finally washed two or three times with alcohol and two or three times with ether (quite neutral), the tube being then dried rapidly in the oven and gently heated with a flame while a moderately rapid current of air is drawn through it.

A current of hydrogen is then passed through the tube and the cupric oxide gently heated over a small flame until it is completely reduced to metallic copper and water no longer condenses in the cold part of the tube. The latter is allowed to cool with the hydrogen still passing and is placed in a desiccator for a time and then weighed. From the weight of the copper obtained, that of the sugar present is deduced by means of tables.

FIG. 48

The filtering tube (Fig. 48) consists of a hard glass tube about 12 cm. in length and 2 cm. in diameter, with a constriction in the middle portion, and drawn off to a tapering tube, 8–10 cm. long, cut obliquely. A cone of platinum gauze is placed on the constriction and then a layer of about 2 cm. of asbestos. The latter is first washed in the hot with caustic soda, hydrochloric acid, nitric acid, and water successively ; it is then poured in the form of an aqueous paste into the tube and washed with a large quantity of water with the help of a pump ; after being washed with alcohol and ether, dried in an oven and gently heated to constant weight, the tube is ready for use. The tube, thus prepared and weighed, is fitted in the rubber stopper of a thick-walled conical flask provided with a side-tube for attachment to a water-pump ; the top of the tube is closed with a cork traversed by a small funnel. The tube is half filled with water, the pump started and the Fehling's solution with the cuprous oxide filtered.

2. DETERMINATION OF THE DIFFERENT SUGARS.

(a) *Glucose.*—60 c.c. of the mixed Fehling's solution and 60 c.c. of water are together heated to boiling, and 25 c.c. of the sugar solution (containing not more than 1% of glucose) added. The liquid is then boiled for 2 minutes and filtered as described above. The weight of glucose present is found from Table XII.

(b) *Levulose.* The procedure is as with glucose, Hönig and Jesser's table [1] being used.

(c) *Invert sugar.* 50 c.c. of Fehling's solution and a volume of the solution containing not more than 0·245 gram of invert sugar are together made up with water to 100 c.c., the liquid being then heated to boiling and the boiling maintained for 2 minutes. The results are calculated from Table XIII.

(d) *Maltose.* A mixture of 50 c.c. of Fehling's solution and 25 c.c. of a maltose solution containing not more than 1% of the sugar is kept boiling for 4 minutes ; *see* Table XIV.

(e) *Lactose.* A mixture of 50 c.c. of Fehling's solution with a volume of the lactose solution containing not more than 0·3 gram of the sugar is made up to 150 c.c. with water, heated to boiling and kept boiling for 6 minutes. Table XV gives the amount of hydrated lactose ($C_{12}H_{22}O_{11}$ + H_2O).

TABLE XII

Glucose corresponding with the Copper weighed (Allihn)

Copper mgrms.	Glucose mgrms.	Copper mgrms.	Glucose mgrms.	Copper mgrms.	Glucose mgrms.	Copper mgrms.	Glucose mgrms.	Copper mgrms.	Glucose mgrms.
10	6·1	105	53·5	200	102·6	290	151·0	380	201·4
15	8·6	110	56·0	205	105·3	295	153·8	385	204·3
20	11·0	115	58·6	210	107·9	300	156·5	390	207·1
25	13·5	120	61·1	215	110·6	305	159·3	395	210·0
30	16·0	125	63·7	220	113·2	310	162·0	400	212·9
35	18·5	130	66·2	225	115·9	315	164·8	405	215·8
40	20·9	135	68·8	230	118·5	320	167·5	410	218·7
45	23·4	140	71·3	235	121·2	325	170·3	415	221·6
50	25·9	145	73·9	240	123·9	330	173·1	420	224·5
55	28·4	150	76·5	245	126·6	335	175·9	425	227·5
60	30·8	155	79·1	250	129·2	340	178·7	430	230·4
65	33·3	160	81·7	255	131·9	345	181·5	435	233·4
70	35·8	165	84·3	260	134·6	350	184·3	440	236·3
75	38·3	170	86·9	265	137·3	355	187·2	445	239·3
80	40·8	175	89·5	270	140·0	360	190·0	450	242·2
85	43·4	180	92·1	275	142·8	365	192·9	455	245·2
90	45·9	185	94·7	280	145·5	370	195·7	460	248·1
95	48·4	190	97·3	285	148·3	375	198·6	465	251·1
100	50·9	195	100·0						

[1] *Zeitschr. des Ver. für die Rübenzuckerind.*, 1888, XXXVIII, p. 1036.

TABLE XIII

Invert Sugar corresponding with the Copper weighed (Meissl)

Copper mgrms.	Invert Sugar mgrms.	Copper mgrms.	Invert Sugar mgrms.	Copper mgrms.	Invert Sugar mgrms.	Copper mgrms.	Invert Sugar mgrms.	Copper mgrms.	Invert Sugar mgrms.
90	46·9	160	84·3	230	123·2	300	163·8	370	206·1
95	49·5	165	87·0	235	126·0	305	166·8	375	209·2
100	52·1	170	89·7	240	128·9	310	169·7	380	212·4
105	54·8	175	92·4	245	131·8	315	172·7	385	215·5
110	57·5	180	95·2	250	134·6	320	175·6	390	218·7
115	60·1	185	97·8	255	137·5	325	178·6	395	221·8
120	62·8	190	100·6	260	140·4	330	181·6	400	224·9
125	65·5	195	103·4	265	143·2	335	184·7	405	228·6
130	68·1	200	106·3	270	146·1	340	187·8	410	232·1
135	70·8	205	109·1	275	149·0	345	190·8	415	235·7
140	73·5	210	111·9	280	151·9	350	193·8	420	239·2
145	76·1	215	114·7	285	154·9	355	196·8	425	242·7
150	78·9	220	117·5	290	157·8	360	199·8	430	246·3
155	81·6	225	120·4	295	160·8	365	203·0		

TABLE XIV

Maltose corresponding with the Copper weighed (Wein)

Copper mgrms.	Maltose mgrms.	Copper mgrms.	Maltose mgrms.	Copper mgrms.	Maltose mgrms.	Copper mgrms.	Maltose mgrms.	Copper mgrms.	Maltose mgrms.
30	25·3	85	73·2	140	122·4	195	171·6	250	220·8
35	29·6	90	77·7	145	126·9	200	176·1	255	225·3
40	33·9	95	82·1	150	131·4	205	180·5	260	229·8
45	38·3	100	86·6	155	135·9	210	185·0	265	234·3
50	42·6	105	91·0	160	140·4	215	189·5	270	238·8
55	47·0	110	95·5	165	144·9	220	193·9	275	243·3
60	51·3	115	99·9	170	149·4	225	198·4	280	247·8
65	55·7	120	104·4	175	153·8	230	202·9	285	252·2
70	60·1	125	108·9	180	158·3	235	207·4	290	256·6
75	64·5	130	113·4	185	162·7	240	211·8	295	261·1
80	68·9	135	117·9	190	167·2	245	216·3	300	265·5

TABLE XV

Lactose (Hydrate) corresponding with the Copper weighed (Soxhlet)

Copper mgrms.	Lactose mgrms.	Copper mgrms.	Lactose mgrms.	Copper mgrms.	Lactose mgrms.	Copper mgrms.	Lactose mgrms.	Copper mgrms.	Lactose mgrms.
100	71·6	165	120·2	225	165·7	285	212·3	345	259·8
105	75·3	170	123·9	230	169·4	290	216·3	350	263·9
110	79·0	175	127·8	235	173·1	295	220·3	355	268·0
115	82·7	180	131·6	240	176·9	300	224·4	360	272·1
120	86·4	185	135·4	245	180·8	305	228·3	365	276·2
125	90·1	190	139·3	250	184·8	310	232·2	370	280·5
130	93·8	195	143·1	255	188·7	315	236·1	375	284·8
135	97·6	200	146·9	260	192·5	320	240·0	380	289·1
140	101·3	205	150·7	265	196·4	325	243·9	385	293·4
145	105·1	210	154·5	270	200·3	330	247·7	390	297·7
150	108·8	215	158·2	275	204·3	335	251·6	395	302·0
155	112·6	220	161·9	280	208·3	340	255·7	400	306·3
160	116·4								

3. Volumetric Determination of Sugars with Fehling's Solution.[1]— This method consists in determining the quantity of substance which completely reduces a given volume of Fehling's solution. The solution of the reducing sugar used contains 0·5–1% of the sugar. Into several similar flasks are measured equal volumes of Fehling's solution, which is sometimes left undiluted, but is more frequently mixed with 4 vols. of water; various tests are then made to ascertain the volume of sugar solution necessary to reduce completely the amount of Fehling's solution employed. As a rule, 10 c.c. of Fehling's solution (5 c.c. of copper solution + 5 c.c. of alkaline tartrate) and 40 c.c. of water are taken.[2]

The flask containing the Fehling's solution is heated on a wire gauze and, when the liquid begins to boil, a certain volume of the sugar solution is run in from a burette. The solution is again heated to boiling and kept boiling for the requisite time (2 minutes for glucose, levulose or invert sugar, 4 for maltose and 6 for lactose), at the end of which the flask is removed from the flame and a few drops of the liquid immediately filtered through a double filter into a test-tube, acidified with acetic acid and tested with a drop of potassium ferrocyanide solution. The formation of a red coloration or precipitate due to the presence of copper indicates that the Fehling's solution is not entirely reduced, so that in the succeeding test a larger amount of the sugar solution is taken. If, however, no reaction for copper is obtained with the filtrate, a smaller volume of the sugar solution is used for the next test. Increase or decrease of the amount of sugar solution

[1] See also : Ling and his Collaborators, *The Analyst*, 1905, XXX, p. 182 ; 1908, XXXIII, pp. 160, 167.

[2] When various successive tests are to be made, it is obvious that greater accuracy in the measurement of the volumes may be attained by preparing a quantity of the diluted Fehling's solution (e.g., 50 c.c. of each of the two liquids + 400 c.c. of water) and taking 50 c.c. of the mixture for each test. The two liquids should be well mixed before dilution with the water and the diluted solution should not be kept from one day to the next.

TABLE XVI

Polarimetric and Reducing Constants of the Principal Sugars

Sugar.	Specific Rotation $[\alpha]_D^{20}$	Grams per 100 c.c. to give rotation of			Rotation due to 1 gram per 100 c.c.			Grams to reduce 100 c.c. of Fehling's Solution.		C.c. of Fehling's Solution reduced by 1 gram.	
		1 Circular Degree (true c.c.).	1 Ventzke Division (true c.c.).	1 Ventzke Division (Mohr c.c.).	Circular Degrees (true c.c.).	Ventzke Divisions (true c.c.).	Ventzke Divisions (Mohr c.c.).	Undiluted.	Diluted with 4 vols. of Water.	Undiluted.	Diluted with 4 vols. of Water.
Saccharose . . .	+ 66·5	0·7519	0·26000	0·26048	1·330	3·846	3·839	—	—	—	—
Invert sugar . . .	− 20·2	2·475	0·8380	0·8395	− 0·404	− 1·193	− 1·191	0·494	0·515	202·4	194
Glucose	+ 52·8	0·947	0·3275	0·3281	1·056	3·053	3·048	0·475	0·4945	210·4	202·2
Levulose. . . .	− 93·0	0·5376	0·1838	0·1841	− 1·860	− 5·439	− 5·430	0·514	0·537	194·4	186
Maltose . . .	+ 138·2	0·3618	0·1255	0·1258	2·764	7·968	7·949	0·779	0·741	128·4	135
Lactose (hydrated) .	+ 52·53	0·9518	0·3288	0·3295	1·051	3·041	3·035	0·676	0·676	148	148
Raffinose (hydrated) .	+ 104·5	0·4785	0·16545	0·16576	2·090	6·044	6·033	—	—	—	—
,, (anhydrous).	+ 123·1	0·406	0·14039	0·14065	2·463	7·123	7·110	—	—	—	—

taken is continued until, in the one case, the reaction for copper fails or, in the other, makes its appearance, in the filtrate. In practice it is convenient to use first an insufficient volume of sugar solution and to continue adding the latter to the same flask and boiling afresh until the filtered liquid no longer gives the copper reaction. On the basis of the approximate result thus obtained it is possible, after a few trials, to obtain two tests in which the volumes of sugar solution employed differ by 0·1 c.c., while only one of them gives a filtrate containing copper. The mean of the two volumes is taken as correct.

If a is the number of c.c. of sugar solution used to reduce completely 10 c.c. of Fehling's solution (diluted with 40 c.c. of water) and f the number of grams of the particular reducing sugar which reduce 100 c.c. of Fehling's solution (under the same conditions of dilution), then the quantity x of the reducing sugar in 100 c.c. of the sugar solution used will be given by :

$$x = \frac{10\,f}{a}.$$

The values of f are given in Table XVI, which contains also the polarimetric data for the various sugars (referred to 20° C., a tube 20 cm. in length, and the ordinary concentrations ; *see* above : Optical Method).

5. Determination of the Sugars in their Mixtures.

1. Fundamental Principles.—The determination of two or more sugars present in a mixture is usually carried out by indirect methods, based on : (1) the rotatory powers, (2) the reducing powers, and (3) the transformation of certain sugars into others by *inversion*, which is effected by dilute acids or special enzymes. From the rotatory and reducing powers of the mixture, in some cases both before and after inversion, the quantity of each sugar in the mixture is calculated.

The determination of the rotatory and reducing powers has already been described. The method of inversion will now be considered (*see* 2) and the various typical cases (3–8) which may present themselves in the analysis of mixtures of sugars.

2. Inversion.—The principal sugars undergoing inversion are saccharose, lactose and raffinose. ·With saccharose, the procedure is as follows :

The saccharose solution to be inverted (containing one-half of the normal weight in about 75 c.c. of water) is mixed in a 100 c.c. flask with 5 c.c. of hydrochloric acid (sp. gr. 1·188), a thermometer being inserted in the flask and the latter placed in a water-bath at 70°. After the temperature of the sugar solution reaches 67–70°, it is maintained at this point for exactly 5 minutes, with frequent shaking ; the whole period of immersion in the bath never exceeds 10 minutes. The flask is subsequently cooled rapidly under the tap, the thermometer withdrawn and washed into the flask, and the solution neutralised almost completely with potassium hydroxide solution.[1]

[1] The above procedure is adopted for the inversion of saccharose solutions of about the concentration indicated ; with more dilute solutions, inversion may also be carried out by adding 5 c.c. of hydrochloric acid (sp. gr. 1·10) to about 50 c.c. of the solution to be inverted and heating for 15 minutes in a water-bath at 67–70° (*see*, for instance, determination of sugars in the chapters on milk and on wine).

By this means the saccharose is converted completely into invert sugar ; lactose and maltose, however, are not changed, as their inversion requires either more concentrated acid or more prolonged boiling. Raffinose undergoes partial inversion, being transformed into a mixture of levulose and melibiose, while its rotation is reduced to about one-half (exactly $0 \cdot 5124$) of that of the same solution before inversion ; only by further action of more concentrated acid ·is the melibiose decomposed into glucose and galactose.

3. Determination of Saccharose and a Reducing Sugar together.— This is the simplest case and if the mixture contains no substances other than the two sugars, it is sufficient to determine the polarisation P given by a solution of p grams of the mixture in 100 c.c. Then, if a_1 and a_2 are the deviations due to unit weight of saccharose and the other sugar respectively in 100 c.c.—due attention being paid to the sign [1]—and x and y the quantities of saccharose and of the other sugar, the following equations hold :

(I)
$$\begin{cases} x + y = p \\ a_1 x + a_2 y = P \end{cases}$$

which give :

(II)
$$x = \frac{P - a_2 p}{a_1 - a_2} ; \quad y = \frac{a_1 p - P}{a_1 - a_2}.$$

When, however, the material to be examined contains also other substances, the first equation no longer holds, and to obtain another, use is made of either the reducing power or inversion, according to one of the th e following methods :

(a) The quantity of reducing sugar is determined directly, either volumetrically or gravimetrically ; the observed polarisation is then diminished by that due to the reducing sugar found, the remainder being the polarisation of the saccharose. That is, in equation

$$a_1 x + a_2 y = P,$$

y becomes known, so that :

$$x = \frac{P - a_2 y}{a_1}.$$

This procedure does not, however, take into account the slight variation in the reducing power of sugars in presence of saccharose.[2]

(b) The saccharose is inverted in the manner already described, and

[1] In the application of these and all the succeeding formulæ to practical cases, the proper sign (+ or −) should always be used for the unit deviations (a) and the observed polarisations (P).

Further, if the mean values of Table XVI are taken for the unit deviations, variation of these with the concentration is not allowed for, while, if the temperature exerts an appreciable influence on the rotation it is presumed that the polarimetric readings are made at 20° C.

[2] This variation is allowed for in some special cases, as in the determination of small quantities of invert sugar in presence of excess of saccharose according to Herzfeld's and Meissl's methods, which will be described under " Raw Sugars."

The method described above is, however, followed, e.g., in the determination of the sugars of condensed milk according to Girard's method (see under " Milk ").

the polarisation before (P) and after inversion (P_1)—referred to the original concentration—determined; if, then, α_3 is the deviation given by unit weight of the inverted sugar in 100 c.c., it follows, since 1 gram of saccharose yields 1·053 gram of invert sugar, that:

(III)
$$\begin{cases} \alpha_1 x + \alpha_2 y = P \\ 1·053\, x + \alpha_2 y = P_1, \end{cases}$$

which give:

(IV)
$$x = \frac{P - P_1}{\alpha_1 - 1·053\, \alpha_3}$$

$$y = \frac{\alpha_1 P_1 - 1·053\, \alpha_3 P}{\alpha_2 (\alpha_1 - 1·053\, \alpha_3)}.$$

The introduction into these formulæ of the values of α_1 and α_3 for the Ventzke scale polarimeter (*see* Table XVI), namely, $\alpha_1 = 3·839$ and $\alpha_3 = -1·191$ (Mohr c.c.) or $\alpha_1 = 3·846$ and $\alpha_3 = -1·193$ (true c.c.), gives:

Mohr c.c.   True c.c.

(V
$$x = \frac{P - P_1}{5·093} \qquad\qquad x = \frac{P - P_1}{5·102}$$

$$y = \frac{3·839\, P_1 + 1·254\, P}{5·093\, \alpha_2} \qquad y = \frac{3·846\, P_1 + 1·256\, P}{5·102\, \alpha_2}.$$

Since, in the formula for x, α_2 does not appear, the same result is obtained for definite values of P and P_1 whatever the sugar (reducing and non-invertible) accompanying the saccharose.

If the polarimetric observations are made at a temperature t differing from 20°, allowance must be made for the variation of the rotatory power, especially for invert sugar; in such cases, formula V is replaced by Clerget's formula [1]:

Mohr c.c.   True c.c.

(VI)
$$x = \frac{26·048\ (P - P_1)}{142·66 - 0·5\, t} \qquad x = \frac{26\ (P - P_1)}{142·66 - 0·5\, t},$$

which are readily understood when it is observed that the denominator is

[1] In Clerget's formula, the variation of the rotation of invert sugar with the concentration is disregarded. To allow for this, the constant 142·66 is replaced by a constant, $C = 141·78 + 0·0676\, s$, where s is the quantity of saccharose contained in the volume of solution subjected to inversion. The values of C determined by this formula are given in the following table (*see* Herzfeld : *Zeitschr. des Ver. für die Rüben-zuckerind.*, 1890, pp. 203-206 ; *Zeitschr. des Ver. der deutschen Zuckerind.*, 1903, I, pp. 555-556) :

Grams of Sugar.	Values of C.	Grams of Sugar.	Values of C.	Grams of Sugar.	Values of C.
1	141·85	6	142·18	10	142·46
2	141·91	7	142·25	11	142·52
3	141·98	8	142·32	12	142·59
4	142·05	9	142·39	13	142·66
5	142·12				

the algebraic difference between the rotation given by the normal weight of saccharose in 100 c.c. and that given by the same solution after inversion :

$$100 - (-42.66 + 0.5\ t) = 142.66 - 0.5\ t.$$

For $t = 20$, this formula is identical with the first of formulæ V.

Formulæ V and VI give the quantities of the two sugars in p grams of the substance dissolved in 100 c.c. The respective percentages, X and Y, are given by :

$$\text{(VII)} \qquad X = \frac{100\ x}{p} \quad \text{and} \quad Y = \frac{100\ y}{p}.$$

It is easy to see that if the normal weight of the substance is taken (i.e., $p = 26.048$ or 26), Clerget's formula becomes :

$$\text{(VIII)} \qquad X = \frac{100\ (P - P_1)}{142.66 - 0.5\ t}.$$

As regards the second formula (V), which gives the quantity y of the reducing sugar accompanying the saccharose, insertion of the various values for α_2 on the Ventzke scale (see Table XVI) gives the following results :

	Mohr c.c.	True c.c.
Glucose . . .	$\dfrac{3.839\ P_1 + 1.254\ P}{15.523}$	$\dfrac{3.846\ P_1 + 1.256\ P}{15.576}$
Levulose . . .	$\dfrac{-3.839\ P_1 - 1.254\ P}{27.655}$	$\dfrac{-3.846\ P_1 - 1.256\ P}{27.750}$
Invert Sugar . .	$\dfrac{-3.839\ P_1 - 1.254\ P}{6.066}$	$\dfrac{-3.846\ P_1 - 1.256\ P}{6.087}$
Maltose . . .	$\dfrac{3.839\ P_1 + 1.254\ P}{40.484}$	$\dfrac{3.846\ P_1 + 1.256\ P}{40.653}$
Lactose . . .	$\dfrac{3.839\ P_1 + 1.254\ P}{15.457}$	$\dfrac{3.846\ P_1 + 1.256\ P}{15.515}$

If the percentage of the reducing sugar is required, the second formula VII is applied.

Instead of one of the methods (a) and (b), a mixed procedure is often followed in practice, the reducing sugar being determined by means of Fehling's solution and the saccharose by Clerget's method [1] :

(c) The reducing sugar accompanying the saccharose is determined directly by Fehling's solution. The saccharose is then inverted and the reducing power again determined. The difference between the two results gives the invert sugar derived from the saccharose and hence, by multiplying by 0.95, the saccharose itself.[2]

This method involves a source of error in cases where the reducing sugar

[1] This is the procedure employed in the analysis of many products containing sugar (see later in this chapter) and of spirituous liquors, in the determination of saccharose and lactose in condensed milk (q.v.), etc.

[2] This method is often used with products containing sugar (see later in this chapter), with wines, etc., to confirm the proportion of saccharose found polarimetrically.

accompanying the saccharose requires boiling for more than two minutes for its determination with Fehling's solution.   In such cases the boiling should be prolonged for the maximum time required, since protraction of the boiling does not alter the results appreciably, whilst with insufficient boiling the reduction is incomplete.

4. Determination of Saccharose and Raffinose together.—The above methods are not available in this case, since raffinose undergoes inversion and is non-reducing. The polarisations before (P) and after inversion (P_1) are determined ; if a_1 and a_2 are the respective rotations due to unit weight of the two sugars in 100 c.c., and a_3 and a_4 the corresponding rotations after inversion, then, since 1 gram of raffinose furnishes under the conditions of inversion already indicated 1·036 gram of inversion products, it follows that :

$$\textbf{(IX)} \qquad \begin{cases} a_1\,x + a_2\,y = P \\ 1\!\cdot\!053\,a_3\,x + 1\!\cdot\!036\,a_4\,y = P_1. \end{cases}$$

By introduction of the values of a_1 and a_2 (for anhydrous raffinose) and a_3 for the Ventzke scale (*see* Table XVI) and placing $1\!\cdot\!036\,a_4 = 0\!\cdot\!5124\,a_2$ (*see* p. 115), these equations become :

Mohr c.c.

$$\begin{cases} 3\!\cdot\!839\,x + 7\!\cdot\!11\,y \ = P \\ -1\!\cdot\!254\,x + 3\!\cdot\!643\,y = P_1 \end{cases}$$

True c.c.

$$\begin{cases} 3\!\cdot\!846\,x + 7\!\cdot\!123\,y = P \\ -1\!\cdot\!256\,x + 3\!\cdot\!650\,y = P_1 \end{cases}$$

These give :

$$x = \frac{0\!\cdot\!5124\,P - P_1}{3\!\cdot\!221}$$

$$y = \frac{P - 3\!\cdot\!839\,x}{7\!\cdot\!11} = \frac{1\!\cdot\!254\,P + 3\!\cdot\!839\,P_1}{22\!\cdot\!9}$$

$$x = \frac{0\!\cdot\!5124\,P - P_1}{3\!\cdot\!227}$$

$$y = \frac{P - 3\!\cdot\!846\,x}{7\!\cdot\!123} = \frac{1\!\cdot\!256\,P + 3\!\cdot\!846\,P_1}{23}$$

If the solutions used contain the normal weight of the substance in 100 c.c., the percentages of saccharose (X) and raffinose (Y) in the substance are obtained by dividing x and y by 0·26048 or 0·26, so that :

$$X = \frac{0\!\cdot\!5124\,P - P_1}{0\!\cdot\!839}; \quad Y = \frac{P - X}{1\!\cdot\!852},$$

which are valid for either Mohr or true c.c.   Introduction of the value of x into the second of these equations gives :

Mohr c.c

$$Y = \frac{1\!\cdot\!254\,P + 3\!\cdot\!839\,P_1}{5\!\cdot\!965}$$

True c.c.

$$Y = \frac{1\!\cdot\!256\,P + 3\!\cdot\!846\,P_1}{5\!\cdot\!976}.$$

5. Determination of two Reducing Sugars together.—If the mixture to be examined contains no substance other than the two sugars and if the rotations of these are not nearly equal, it is sufficient to determine the polarisation and to apply the two equations (I) and the formulæ (II) already given for the case of mixtures of saccharose with another sugar, a_1 and a_2 now indicating the rotations due to unit weights of the two sugars in 100 c.c. and x and y their respective quantities.

If, however, the substance contains also non-saccharine substances, it

becomes necessary to determine also the reducing power of the substance. If β_1 and β_2 indicate the number of c.c. of Fehling's solution reduced by unit weight of each of the two sugars dissolved in 100 c.c. (from Table XVI) and F the number of c.c. of Fehling's solution reduced by the weight p of the substance used for the analysis,[1] then :

(X)
$$\begin{cases} a_1 x + a_2 y = P \\ \beta_1 x + \beta_2 y = F \end{cases}$$

which give :

(XI)
$$x = \frac{\beta_2 P - a_2 F}{a_1 \beta_2 - a_2 \beta_1} \text{ and } y = \frac{a_1 F - \beta_1 P}{a_1 \beta_2 - a_2 \beta_1}.$$

This procedure assumes, however, that the volume of Fehling's solution reduced by each sugar is proportional to its quantity, which is rigorously exact only within very narrow limits ; it neglects, indeed, causes of error arising from the influence of one sugar on the reducing power of the other and from the necessary duration of the boiling with Fehling's solution, which is not the same for all sugars.

In the principal practical cases, the formulæ (XI) give, when the Ventzke scale values of a_1 and a_2, and the values of β_1 and β_2 are inserted, the following results :

	Mohr c.c.	True c.c.
Glucose (x) and levulose (y)	$x = \dfrac{186\, P + 5\cdot430\, F}{1665}$ $y = \dfrac{3\cdot048\, F - 202\cdot2\, P}{1665}$	$\dfrac{186\, P + 5\cdot439\, F}{1668}$ $\dfrac{3\cdot053\, F - 202\cdot2\, P}{1668}$
Invert sugar (x) and glucose (y)	$x = \dfrac{3\cdot048\, F - 202\cdot2\, P}{832}$ $y = \dfrac{194\, P + 1\cdot191\, F}{832}$	$\dfrac{3\cdot053\, F - 202\cdot2\, P}{833}$ $\dfrac{194\, P + 1\cdot193\, F}{833}$
Invert sugar (x) and levulose (y)	$x = \dfrac{186\, P + 5\cdot430\, F}{832}$ $y = \dfrac{-194\, P - 1\cdot191\, F}{832}$	$\dfrac{186\, P + 5\cdot439\, F}{833}$ $\dfrac{-194\, P - 1\cdot193\, F}{833}$
Glucose (x) and maltose (y)	$x = \dfrac{7\cdot949\, F - 135\, P}{1196}$ $y = \dfrac{202\cdot2\, P - 3\cdot048\, F}{1196}$	$\dfrac{7\cdot968\, F - 135\, P}{1199}$ $\dfrac{202\cdot2\, P - 3\cdot053\, F}{1199}$
Invert sugar (x) and maltose (y)	$x = \dfrac{7\cdot949\, F - 135\, P}{1703}$ $y = \dfrac{1\cdot191\, F + 194\, P}{1703}$	$\dfrac{7\cdot968\, F - 135\, P}{1707}$ $\dfrac{1\cdot193\, F + 194\, P}{1707}$

[1] If a c.c. of the sugar solution (p grams in 100 c.c.) diluted n times, reduce 10 c.c. of Fehling's solution (diluted with 4 vols. of water), F is given by the expression :

$$F = \frac{1000\, n}{a}$$

	Mohr c.c.	True c.c.

$$\text{Glucose } (x) \text{ and lactose } (y) \begin{cases} x = \dfrac{3 \cdot 035\,F - 148\,P}{162 \cdot 6} & \dfrac{3 \cdot 041\,F - 148\,P}{163} \\[2ex] y = \dfrac{202 \cdot 2\,P - 3 \cdot 048\,F}{162 \cdot 6} & \dfrac{202 \cdot 2\,P - 3 \cdot 053\,F}{163} \end{cases}$$

$$\text{Invert sugar } (x) \text{ and lactose } (y) \begin{cases} x = \dfrac{3 \cdot 035\,F - 148\,P}{765} & \dfrac{3 \cdot 041\,F - 148\,P}{766 \cdot 5} \\[2ex] y = \dfrac{1 \cdot 191\,F + 194\,P}{765} & \dfrac{1 \cdot 193\,F + 194\,P}{766 \cdot 5} \end{cases}$$

The second and third cases—mixtures of invert sugar with excess of glucose or levulose—may be reduced to the first case—mixtures of glucose and levulose.[1]

6. Determination of Saccharose and two Reducing Sugars together.—Let x, y and z be the respective quantities of the three sugars contained in the weight p of substance dissolved in 100 c.c. ; a_1, a_2 and a_3 the rotations due to 1 gram of each sugar in 100 c.c., a_4 that due to 1 gram of invert sugar, and β_2 and β_3 the numbers of c.c. of Fehling's solution reduced by 1 gram of each of the two reducing sugars present ; P and P_1 the polarisations before and after inversion and F the number of c.c. of Fehling's solution reduced by the weight p of the substance.   The following equations may then be established :

$$(\text{XII}) \qquad \begin{cases} a_1 x + a_2 y + a_3 z = P \\ 1 \cdot 053\,a_4 x + a_2 y + a_3 z = P_1 \\ \beta_2 y + \beta_3 z = F \end{cases}$$

The first two give :

$$x = \frac{P - P_1}{a_1 - 1 \cdot 053\,a_4},$$

which is identical with the first equation IV.   The saccharose is thus calculated as when mixed with only one reducing sugar, i.e., with the first equation V or with that of Clerget (VI or VIII).   When x is found, equations XII give :

$$\begin{cases} a_2 y + a_3 z = P - a_1 x \\ \beta_2 y + \beta_3 z = F \end{cases}$$

which are analogous to X and permit of the determination of y and z.

Introduction into these equations of the values of a_1, a_2, a_3, β_2, β_3 and x for some of the more important practical cases of mixtures of saccharose with different reducing sugars gives the following results [2] :

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[1] A method of this kind is used for the determination of sugars in wine (q.v.).

[2] A procedure of this kind, with slight variations, is applied to the analysis of wines containing saccharose and also of condensed milk in which invert sugar as well as saccharose is present ; this is described in dealing with these products.

	Mohr c.c.	True c.c.

Glucose (y) and levulose (z)

$$y = \frac{233\,P + 714\,P_1 + 27{\cdot}65\,F}{8479} \qquad \frac{233{\cdot}6\,P + 715\,P_1 + 27{\cdot}7\,F}{8508}$$

$$z = \frac{15{\cdot}52\,F - 253{\cdot}6\,P - 776\,P_1}{8479} \qquad \frac{15{\cdot}58\,F - 254\,P - 778\,P_1}{8508}$$

Glucose (y) and lactose (z)

$$y = \frac{15{\cdot}46\,F - 185{\cdot}6\,P - 568\,P_1}{828} \qquad \frac{15{\cdot}52\,F - 186\,P - 569\,P_1}{831{\cdot}6}$$

$$z = \frac{253{\cdot}6\,P + 776\,P_1 - 15{\cdot}52\,F}{828} \qquad \frac{254\,P + 778\,P_1 - 15{\cdot}58\,F}{831{\cdot}6}$$

Invert sugar (y) and lactose (z)

$$y = \frac{15{\cdot}46\,F - 185{\cdot}6\,P - 568\,P_1}{3896} \qquad \frac{15{\cdot}52\,F - 186\,P - 569\,P_1}{3911}$$

$$z = \frac{6{\cdot}066\,F + 243{\cdot}3\,P + 745\,P_1}{3896} \qquad \frac{6{\cdot}087\,F + 243{\cdot}7\,P + 746\,P_1}{3911}$$

7. Determination of Saccharose, Raffinose and a Reducing Sugar together.—If the same notation as before is used and α_5 represent the rotation due to 1 gram of the inversion products of raffinose, the following three equations hold :

$$\text{(XIII)} \qquad \begin{cases} \alpha_1 x + \alpha_2 y + \alpha_3 z = P \\ 1{\cdot}053\,\alpha_4 x + 1{\cdot}036\,\alpha_5 y + \alpha_3 z = P_1 \\ \beta_3 z = F \end{cases}$$

The last equation gives z at once, and the remaining two then become analogous to IX :

$$\begin{cases} \alpha_1 x + \alpha_2 y = P - \alpha_3 z \\ 1{\cdot}053\,\alpha_4 x + 1{\cdot}036\,\alpha_5 y = P_1 - \alpha_3 z. \end{cases}$$

With a mixture of saccharose (x), raffinose (y) and invert sugar (z), introduction of the corresponding values of the constants (*see* above, 4) gives the following results :

Mohr c.c.	True c.c.

$$x = \frac{0{\cdot}5124\,P - P_1 - 0{\cdot}003\,F}{3{\cdot}221} \qquad \frac{0{\cdot}5124\,P - P_1 - 0{\cdot}003\,F}{3{\cdot}227}$$

$$y = \frac{1{\cdot}254\,P + 3{\cdot}839\,P_1 + 0{\cdot}031\,F}{22{\cdot}9} \qquad \frac{1{\cdot}256\,P + 3{\cdot}846\,P_1 + 0{\cdot}031\,F}{23}$$

$$z = \frac{F}{194}.$$

8. Determination of three Reducing Sugars together.—This case, which seldom occurs in practice, can be solved only when no substances other than the three sugars are present, the equations then being :

$$\text{(XIV)} \qquad \begin{cases} x + y + z = p \\ \alpha_1 x + \alpha_2 y + \alpha_3 z = P \\ \beta_1 x + \beta_2 y + \beta_3 z = F \end{cases}$$

which allow of the determination of x, y and z, but leave out of account

the many causes of error, e.g., the influence of one sugar on the reducing powers of the others, the different periods of boiling with Fehling's solution, and the influence of the concentration on the rotatory and reducing powers.

SPECIAL PART

Prime Materials and Products of the Sugar Industry

The prime material of the beetroot sugar industry, which alone is treated here, is the *sugar beet*.[1] From this is extracted by processes usually based on osmotic phenomena the raw or *diffusion juice*, the residues being known as exhausted slices. The raw juice is subjected to an initial purification in which many extraneous matters are precipitated. The resultant *defecated juice* is evaporated to *dense juice* and then under reduced pressure to *masse-cuite*, in which part of the sugar is crystallised, while the remainder is still dissolved as *syrup*. The crystallised *raw sugar* is then refined to *refined sugar*. The syrups are then subjected to further treatment to obtain more sugar, and this process is continued until syrups are left so rich in non-saccharine matters that the sugar can no longer separate by simple crystallisation ; these constitute the *molasses*. Other residues from the manufacture are *waste diffusion liquor*, *filter-press washings* and *sludge* from the defecation of the juice.

Sampling.—A point of the first importance is the preparation of a representative sample. With beets, the sample may be taken in the field, or in the trucks or wagons, or in the factory. In any case, a certain number of the roots, say 25, as nearly as possible of average size and appearance, are chosen. According to some authorities, from each lot of beets (truck, heap or camp) a good number should be collected from points uniformly distributed throughout the mass ; these should then be arranged in order of magnitude and 10 or 20 of them picked out at regular intervals, e.g., every third or every fourth.

The raw juice in the diffusors is not of uniform composition, so that the whole mass should be well mixed before sampling or, if this is not possible, amounts proportional to the bulks in the different parts should be taken and mixed. A similar procedure is followed with the defecated juice, the sample in either case being stored in a tightly stoppered bottle.

The juice should be analysed immediately or, if this is impracticable, a preservative should be added. Basic lead acetate is usually added in the proportion of 1 : 10 for this purpose, the result of the determination of the sugar—which is the only one that can then be carried out—being suitably corrected. Some advise the addition of 1 gram per litre of mercuric chloride or ammonium fluoride, which have no appreciable influence on the specific gravity or on the determination of the sugar ; others add a few drops of formalin, whilst it has been suggested that the juice be sterilised by keeping it in a closed vessel in boiling water for an hour. When, however, the juice

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[1] Analysis of raw and refined cane sugar is carried out like that of raw and refined beet sugar.

has undergone alteration, these means are inadequate to preserve it and the analysis must be made immediately the sample is taken.

With very viscous or semi-solid liquids such as syrups, molasses and massecuite, the sample is taken by means of a cylindrical metal sampler in such a way that proportionate amounts are taken at different depths. With very dense products which may have crystallised sugar at the bottom, it is especially necessary to reach with the sampler the very bottom of the vessel. Several samples are withdrawn and mixed and the sample or samples for analysis (about 200 grams each) then stored in glass bottles with ground stoppers.

With raw sugar in sacks, at least 10 sacks in every 100 are sampled with a semi-cylindrical brass or sheet iron sampler, which is about 80 cm. long and 2 cm. in diameter and ends in a point. This sampler is plunged into the sugar so that it penetrates rather less than half-way and is then extracted and turned meanwhile so that it brings out with it a certain quantity of the sugar. With heaped sugar, samples are taken from the centre and edges of each heap and at different depths.

The different samples are placed separately on a clean, dry table or, better, if the surroundings are very warm, in closed vessels so that loss of moisture may be avoided. The samples are compared to ascertain if they are uniform as regards external characters, such as colour, grain and the like. If this is the case, they are carefully mixed on a wooden table with a clean, dry wooden spatula, all lumps being disintegrated,[1] so that a homogeneous mass of at least a kilogram is obtained. From this, a sample or samples of about 200 grams are taken and kept in tightly closed tins or in ground-stoppered bottles of such size that the sample just fills one.

If, however, the different portions from the sacks or heaps do not appear uniform, separate samples of the different varieties of sugar are taken in the proper amounts and treated as above.

BEET

Beets should be analysed as soon as the sample reaches the laboratory, since they are subject to alteration. All the beets are first weighed together so as to obtain the *mean weight of the beet*. The roots are then carefully cleaned externally, all earthy matter being removed with a brush and, if necessary, by careful washing with cold water (this is to be avoided with split or cracked beets). The roots are at once dried and the tops cut off, the weight being then again determined ; this gives the *mean weight of the cleaned and topped beet*.

All the beets are now halved or quartered by cutting lengthwise, the half or quarter of each root being reduced to pulp by means of a grater or, better, a special machine. A very fine pulp may be obtained from beets already coarsely cut up by presses such as Pellet's " Sans Pareille."

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[1] Some place the lumps on one side and, after weighing them to estimate their percentage of the total, analyse them separately, the analytical results of the sugar being corrected accordingly.

When the beets to be analysed are already in *slices*, these are pulped by a mincing or other machine or by the Pellet press.

On the pulp thus obtained the determinations indicated below are carried out ; if a more detailed analysis is required, part of the pulp is pressed and the *juice* obtained analysed by the methods given in the succeeding article. Both the pulp and the juice should be analysed immediately, as they readily undergo change ; the pulp should be kept in closed vessels to prevent drying.

The pulp is usually analysed for sugar (saccharose), quantity of juice and water.

1. Extraction and Determination of the Sugar.—Of the various methods proposed for the extraction of the sugar from the pulp, the most important are as follows :

(a) ALCOHOLIC EXTRACTION.—This is the most exact method and is always used in scientific investigations. The apparatus consists of a 100 c.c. flask with the neck widened out above the mark and surmounted by a Soxhlet extractor fitted with a vertical bulb condenser (Fig. 49). The extractor should be of such a size that the normal weight, i.e., 26·048 grams (for Mohr c.c.), of the pulp does not reach above the level of the upper bend of the siphon. This quantity of the pulp is weighed in a tared dish and mixed in this with 3 c.c. of basic lead acetate solution [1] and 4–5 c.c. of alcohol by means of a glass rod. The mass is introduced into a filter-paper thimble and the latter placed in the extractor, into which the glass rod and dish are washed with 90% alcohol. According to some, the extraction is facilitated by heating the pulp and basic lead acetate with a little alcohol for a few minutes and then introducing the mass into the extractor.

The flask below the extractor is also charged with 90% alcohol, the total amount of the latter used being about 75 c.c. ; the apparatus is fitted together and the flask heated on a water-bath so that the alcohol boils. The extraction should be complete in about 2 hours. The residue may be extracted with fresh alcohol and the latter tested in the polarimeter, or one or two drops of the alcohol from the extractor may be mixed in a test-tube with 2 c.c. of distilled water and 5 drops of fresh 20% alcoholic a-naphthol and 10 c.c. of concentrated sulphuric acid (free from any trace of nitric acid) added so that the two liquids do not mix ; in presence of sugar a violet ring forms at the surface between the acid and the alcoholic solution.

The alcoholic solution of the sugar is cooled, made up to volume with alcohol, filtered through a dry filter and polarised.

(b) AQUEOUS DIGESTION. Hot or cold digestion is usually employed in practice, cold digestion requiring a very fine pulp such as is obtained from the Pellet press, whereas with hot digestion a coarser pulp suffices. In either case, various methods are available, the principal ones being those of Pellet and of Sachs and Le Docte.

1. *Pellet method.* For hot digestion, 26·048 grams (Mohr c.c.) of the pulp are placed in a 200 c.c. flask, into which the dish is well washed with

[1] This solution is prepared by digesting 300 grams of neutral lead acetate and 100 grams of litharge with a litre of water in the hot, the liquid being filtered after 12 hours and kept in tightly closed bottles. It may also be prepared by digestion in the cold with occasional stirring, several days being required under these conditions.

hot water ; 5 c.c. of basic lead acetate are then added and hot water nearly up to the mark, the mass being mixed and the flask immersed in boiling water for half an hour.   It is then cooled to the standard temperature (17·5° C. for Mohr graduation), the froth removed by addition of a drop or two of ether and made up to the mark, 0·6 c.c. of water being added to compensate for the insoluble matter ; the liquid is well mixed, filtered through a dry filter (covered to prevent evaporation) and polarised ; if a 20 cm. tube is used, the result is multiplied by two to obtain the percentage of saccharose.

When working in the cold, a similar procedure is fol- lowed ; the flask is filled to the extent of about two- thirds and shaken vigorously, the froth being removed with ether and the liquid made up to 200·6 c.c., again shaken, filtered and polarised.   With a very fine pulp it is unnecessary for the liquid to stand before filtration.

2. *Sachs and Le Docte method.*   Use is here made of a suitable metallic, cylindrical vessel closed hermetically. Various types have been proposed and the ordinary pre- serve jar, about 12 cm. high and 7 cm. in diameter, fitted with a pressure cover, may be employed.   For hot diges- tion, the closure of the vessel should be particularly tight so that no loss of steam may occur.   The normal weight of pulp is weighed directly into the vessel and 177 c.c. of water containing basic lead acetate (5 c.c. usually suffice) added by means of a special automatic pipette, it being assumed that the normal weight of pulp contains, on the average, 23 c.c. of juice, the total liquid being thus 200 c.c. ; the vessel is then closed.

With hot digestion, the vessel is shaken, immersed for half an hour in a water-bath at about 80°, cooled, again shaken and opened, the liquid being filtered through a dry filter and polarised.   With cold digestion, the vessel is vigorously shaken without being heated, filtered and polarised.   In either case, the funnel and the collecting vessel are covered during the filtration to prevent evapora-

FIG. 49

tion.   The reading in a 20 cm. tube is multiplied by 2 to obtain the per- centage of saccharose.
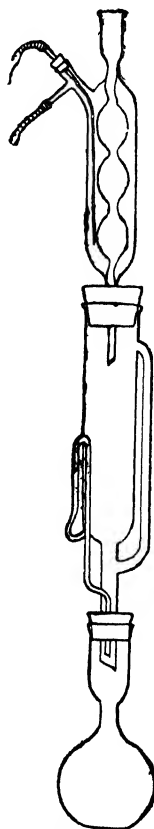
To determine the saccharose in non-exhausted *dry pulp*, such as is obtained by the Steffen process, the following method of aqueous digestion, similar to the Sachs and Le Docte method, may be used [1] : 13·024 grams of the previously comminuted dry pulp are weighed in the metallic vessel, 200 c.c. of water con- taining basic lead acetate (185 c.c. of water + 15 c.c. of the basic acetate) being added and the vessel closed, vigorously shaken and left for 30 minutes.   The liquid is then filtered and polarised in a 40 cm. tube, the percentage of saccharose being given by the formula :

$$S = \frac{P}{200}\left(200 + \frac{13\,a}{100} + \frac{13\,P}{160}\right),$$

[1] Carboni : *Boll. Assoc. It. ind. zucchero e alcool,* 1913–1914, Vol. **vi**, p. 109.

where P is twice the polarimetric reading and a the percentage of water in the pulp.

2. Determination of the Amounts of Juice and Insoluble Matters.—In a large beaker 20 grams of the finely divided pulp are digested with about 400 c.c. of cold water for half an hour, with occasional stirring. The liquid is then filtered with the aid of a pump through either a tared asbestos filter or a filter-paper previously dried at 100–110° to constant weight. The insoluble residue is washed in the beaker with cold water by decantation and then washed completely on to the filter, where it is washed successively with hot water, two or three times with 90% alcohol, and ether. It is then dried at a gentle heat and subsequently at 100–110° to constant weight. Deduction of the percentage of insoluble matter from 100 gives the percentage of juice.

In more exact determinations it is necessary to subtract from the weight of the insoluble matter that of the mineral matter (sand, etc.), to obtain that of the pure cellular substance. For this purpose the filtration should take place through a dried and tared paper, the weighed insoluble matter being afterwards incinerated and the weight of ash subtracted from that of the total insoluble residue.

3. Determination of the Water.—10 grams of the pulp are weighed in a flat porcelain dish, tared along with a glass rod. The drying is carried out first at 50–60° for 2 hours with occasional stirring with the rod, and finally at 110° to constant weight. The loss represents water.

In some cases the pulp, especially if very fine, agglomerates during the drying and loses its water with difficulty ; under these conditions, it is mixed with a known quantity of previously calcined siliceous sand, as with juices.

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Beets contain on the average 4–5% of insoluble matter, and their sugar-content should be at least 12–14% and is often 15–16% and sometimes 20%. Account must, however, also be taken of the quotient of purity of the juice (*see* later).

DIFFUSION JUICES

The indispensable determinations in the analysis of diffusion juices [1] are those of the specific gravity, sugar, water and salts, the non-sugar and the quotient of purity being calculated from these ; in some cases the invert sugar and the acidity are calculated.

1. Determination of the Specific Gravity.—This is carried out as already described (*see* General methods, 1) ; calculation is then made of the degrees Brix, which express the percentage by weight of solid matter in the juice, calculated as though it were all saccharose. Saccharometers give degrees Brix directly.

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[1] Before analysing the juice, if this has been recently obtained, it is well to free it from the air it contains by placing it in a vessel and withdrawing the air from the latter by means of a water-pump until the evolution of bubbles from the liquid ceases ; this requires a few minutes.

The determination of the specific gravity may often be made, with sufficient accuracy, in conjunction with that of the sugar, by weighing the flask empty and then filled with juice to the 50 c.c. or 100 c.c. mark, and dividing the weight of the juice by the volume.

2. Determination of the Sugar.—As it is inconvenient to weigh out exactly the normal weight of the juice, the following procedure is usually preferred : Measuring flasks are used furnished, in addition to the principal mark, with another representing a volume greater by one-tenth, e.g., 50–55, 100–110, 200–220 c.c.

The flask is filled with juice (at 17·5° for Mohr graduations) exactly to the first mark, the amount of basic lead acetate necessary for clarification being added and the volume made up to the second mark with water. After mixing and standing for 10–15 minutes, the liquid is filtered through a dry filter and polarised, the reading being increased by one-tenth and multiplied by 0·26048 to obtain the weight of sugar in 100 c.c. of the juice ; division by the specific gravity gives the percentage by weight :

$$x = \frac{\left(P + \dfrac{P}{10}\right) \times 0\cdot26048}{s},$$

where x = percentage of sugar by weight, P the observed polarisation and s the specific gravity of the juice.[1]

3. Invert Sugar.—This is usually very small in amount with beet juice, and has no sensible influence on the polarimetric determination of the saccharose.

When necessary, it may be determined thus : 250 c.c. of the juice, neutralised exactly with soda solution, are evaporated on a water-bath to 50–60 c.c. and then introduced quantitatively into a 100 c.c. flask, cleared with a little lead acetate, made up to the mark, allowed to settle and filtered. To 80 c.c. of the filtrate, placed in another 100 c.c. flask, is added drop by drop sodium sulphate or phosphate solution until the excess of lead is completely precipitated ; it is then made up to the mark and filtered, and 50 c.c. of the filtrate (corresponding with 100 c.c. of juice) used for the determination of the invert sugar. This may be effected by Herzfeld's method, to be described later (*see* Raw Sugar).

More rapidly, and in most cases with sufficient accuracy, the invert sugar may be determined by the volumetric method, as described in the general methods, but the influence of the large excess of saccharose on the reducing power is then neglected.

4. Water and Dry Matter.—(*a*) *Direct determination.* Into a flat porcelain dish 8–9 cm. in diameter, tared together with a glass rod about 7 cm. long and about 50 grams of washed and calcined coarse sand,[2] are poured 10–12 c.c. of the juice ; after weighing again, the mass is evaporated on a water-bath with frequent mixing. The drying is completed in an

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[1] The calculation may be shortened by using Schmitz's table, which is given in pecial treatises on this subject.

[2] Ground quartz, passing through a 2 mm. sieve but not through a 1·5 mm. sieve, may be used.

oven first for two hours at about 70° and then at 105–110° to constant weight. The residue represents dry matter and the loss in weight, water.

(b) *Indirect determination*. The percentage of water may be deduced with rough approximation by taking as percentage of dry matter the degrees Brix of the juice (*see* above, 1) and subtracting this from 100, i.e., by assuming that the other substances present influence the specific gravity to the same extent as does the saccharose.

Closer approximation is obtained by the refractometric method. For this purpose the refractive index of the juice at 20° is determined, Table X then giving the percentage of sugar, which is regarded as the dry substance; the assumption here made is that the other dissolved matter influences the refractive index to the same extent as the saccharose does.

5. Salts (Ash).—In a platinum dish, 10–20 grams of the juice are evaporated, the residue being moistened with a few drops of concentrated sulphuric acid, heated gently over a small flame until the mass chars and then in direct contact with the flame or in a muffle to complete incineration, care being taken not to heat sufficiently to fuse the ash. The weight of the sulphated salts thus obtained is diminished by one-tenth and calculated as a percentage.

6. Calculation of the Non-sugar.—This is given by the difference between the percentages of dry matter and sugar. If the *total non-sugar* thus found is diminished by the percentage of ash, the *organic non-sugar* is obtained.

7. Calculation of the Quotient of Purity.—From the results of analysis of the juice the percentage of sugar in the dry matter is calculated, this being known as the *quotient* or *coefficient of purity*. If the dry matter has been determined directly, this quotient is known as the *real* coefficient of purity, whereas, if the degrees Brix are taken as the dry matter, it is termed *apparent*. Further, if the dry matter is determined by the refractometric method, the *optical* quotient of purity is obtained, this being also an apparent coefficient, but usually nearer to the real value than the apparent coefficient calculated from the degrees Brix.

8. Acidity.—In unaltered diffusion juices the acidity is mostly very small. When it is necessary to determine it, 100 c.c. of the juice are titrated in presence of a few drops of phenolphthalein with N/10-caustic soda, the result being expressed as grams of calcium oxide required to neutralise 100 c.c. of juice: 1 c.c. N/10-alkali = 0·0028 gram CaO.

* *
* *

With beet juice, attention is paid especially to the percentage of sugar and to the quotient of purity. For a fixed sugar content, juices with the higher quotients of purity give greater yields of the final product. Invert sugar is found in but very small quantity and only in altered juice.

DEFECATED JUICE

In this, besides the specific gravity, sugar, water, non-sugar, salts and quotient of purity—determined as with diffusion juice—estimations of the alkalinity and lime are necessary. As a rule, invert sugar is not determined, as it is not present owing to the alkalinity of the juice.

1. **Alkalinity.**—50 c.c. of the juice are titrated with N/10-sulphuric (or hydrochloric) acid in presence of phenolphthalein, the result being expressed as grams of calcium oxide per 100 c.c. : 1 c.c. N/10-acid = 0·0028 gram CaO. Where many determinations are to be made, an acid is used of such strength that 1 c.c. corresponds with 0·01 or 0·001 gram of CaO (according as the juices are more or less alkaline) when 10 c.c. of the juice are titrated.

2. **Lime.**—This could be determined by precipitation with ammonium oxalate and subsequent titration with permanganate, but in practice use is generally made of Pellet's method, which is carried out as follows :

An alcoholic soap solution (white Marseilles soap in about 60% alcohol, *see* : Water, Vol. I) is prepared of such concentration that 1 c.c. corresponds with 0·0005 gram of CaO. The titre is controlled by means of barium chloride solution containing 0·436 gram of crystallised barium chloride per litre ; 40 c.c. of this solution should require 8 c.c. of the soap solution to form a persistent froth after agitation.

Into a bottle with a ground stopper are poured 20 c.c. of the juice, which is then diluted to about 150 c.c. with distilled water. After addition of a few drops of acetic acid, the liquid is rendered feebly alkaline with ammonia and titrated with the soap solution, which is added until, when the closed bottle is shaken, a froth 1 cm. in height and persisting for at least 10 minutes is obtained. The result is expressed as grams of calcium oxide per 100 c.c. of juice.

* * *

The conclusions to be drawn from the analytical results are as with diffusion juices. The alkalinity and the lime content are of importance since definite limits have been established for them in different cases. Defecated juices should be alkaline, but if the alkalinity is too high, loss of sugar may occur during the subsequent concentration of the juice.

DENSE JUICE AND SYRUP

With these, the principal determinations are the same as with defecated juice and are carried out in the same way (*see* below, 1–6). Sometimes also the colour is required (7).

In some cases invert sugar may be present and, more rarely, raffinose ; for the determination of these, *see* later : Raw Sugar.

1. **Specific Gravity.**—This is measured by means of a hydrometer or, more accurately, by a picnometer. The viscosity renders it difficult to use a Westphal balance.

The degrees Brix may also be determined either directly or after dilution

with an equal or multiple weight of water, the reading being multiplied by the degree of dilution. A hydrometer or Westphal balance may also be used after dilution.

EXAMPLE : 10 grams of a juice were diluted with 90 grams of water, the specific gravity at 17·5° then being 1·0201. This corresponds with 5·1 degrees Brix, so that the original solution would have 51 degrees Brix, which is equivalent to the sp. gr. 1·2383.

2. Sugar.—In a German silver or nickel dish exactly 26·048 grams of the substance (using Mohr graduations) are weighed and are then washed completely into a 100 c.c. flask. Sufficient basic lead acetate is added to precipitate the impurities, the clarification being completed with a little alumina cream (a paste of aluminium hydroxide, freshly prepared and well washed with water by decantation). The solution is then made up to the mark, shaken, allowed to stand, filtered and polarised. The reading gives directly the percentage of sugar in the juice.

When invert sugar and raffinose are present in appreciable proportions, direct polarimetric determination of the saccharose does not give accurate results ; the procedure indicated for molasses (*q.v.*) is then followed.

3. Water and Dry Matter.—A direct or an indirect method may be used.

(*a*) *Direct determination.* The procedure is similar to that given for diffusion juice, but only 3–5 grams of substance are taken and after this is weighed into a dish, previously tared with sand (about 50 grams) and a rod, the dish is placed in an oven for a quarter of an hour until the juice becomes fluid and penetrates the sand. The dish is then removed from the oven, placed on a sheet of smooth paper, and the material carefully mixed with the rod so as to obtain a homogeneous mixture. It is then dried in an oven, first at about 70° and then at 100–110° to constant weight, this usually requiring about 8 hours.

(*b*) *Indirect determination.* The water may be calculated, as in diffusion juice, on the assumption that the dry matter is represented by the degrees Brix or, better, by the percentage of sugar determined refractometrically ; in either case, the water is obtained by deducting the percentage of solid matter from 100.

With liquids which are very dense and highly coloured, or contain solid particles, the refractive index may be determined after dilution of the juice with a known proportion of water ; if a weight p of substance, after dilution with a weight p' of water, gives a refractive index corresponding with $a \%$ of water, the percentage of the latter in the undiluted substance will be $a - \dfrac{(100 - a) \, p'}{p}$.

The accuracy of the results of the refractometric determination diminishes, of course, with increase in the non-saccharine substances contained in the liquid. With very impure products this source of error may be obviated to some extent by diluting, not with water, but with a known weight of pure sugar solution in which the water has been determined with the refractometer. Thus, if a weight p of the substance is mixed with

a weight p' of a pure sugar solution the refractive index of which corresponds with $a'\%$ of water, and if the refractive index of the mixture indicates $a\%$ of water, the percentage of water in the original substance is $a - \dfrac{p'\ (a' - a)}{p}$

4. Salts (Ash).—Determined as with diffusion juice on 2–3 grams of substance, to which sulphuric acid is added directly.

5. Non-sugar and Quotient of Purity.—As with diffusion juice.

6. Alkalinity and Lime.—These are determined as in defecated juice, but for the alkalinity only 20–25 c.c. of juice are taken, and this is then diluted sufficiently to give a slightly coloured liquid. If the juice is so highly coloured that the change of colour with phenolphthalein cannot be detected with certainty, sensitive litmus paper is used and a drop of the liquid removed and tested from time to time during the titration.

In determining the lime, 10 c.c. of the juice are diluted and titrated with the alcoholic soap solution as already described.

In both determinations, the result is sometimes calculated with reference to 100 grams and not to 100 c.c. ; the substance used should then be weighed.

7. Colour.—This is measured by means of a colorimeter, such as that of Stammer (*see* Mineral Oils, Vol. I) or Duboscq (*see* Wines, this volume).

With the former instrument, comparison is made with a double disc of yellow glass of definite depth of colour (*standard colour*), and when a 100 mm. layer of a liquid corresponds in colour with the standard, the colour of the liquid is taken as 1 ; thus, the colour of any liquid is obtained by dividing 100 by the depth in mm. of the layer necessary to equal the standard colour. The value obtained is then referred to 100 of pure sugar, allowance being made for the sugar content of the juice and for the extent to which it is diluted for the determination of the colour.

With the Duboscq colorimeter, comparison is made with a standard liquid, but the nature of this has not been definitely fixed ; some use solutions of caramelised sugar of given colouring intensity, others a 0·1%-iodine solution.

MASSECUITE

Since these products are non-homogeneous and contain crystallised sugar in suspension, it is necessary, in order to obtain trustworthy results, to mix the sample well and to take as nearly as possible proportionate quantities of crystals and liquid.

The determinations to be made are the same as for syrups and are made in the same way. As regards the *specific gravity*, for industrial purposes only an approximate value is often required, and this is obtained by weighing the amount of massecuite required to fill a large receptacle, e.g., a bucket of known volume. When, however, an exact value is desired for laboratory purposes, the method indicated below for molasses is used.

MOLASSES

The determinations to be made in this case are the same as for dense juice or massecuite, those of the sugar, water and quotient of purity being especially important. As regards the methods used, the measurements of the specific gravity, water and sugar merit special mention, whilst for the other determinations reference may be made to the part dealing with massecuite. In some instances, determinations of the invert sugar and raffinose are necessary; *see* later: Raw Sugar.

1. Specific Gravity.—The air-bubbles and any suspended solid matter must first be eliminated.

This is best effected by heating the molasses in a hot-water funnel plugged at the bottom, the molasses becoming more fluid when heated and the air-bubbles then rising to the surface together with most of the suspended foreign matters, which form a thick scum and thus prevent evaporation; sand and other heavy particles settle to the bottom. The first portion with the sand, etc., is then run off and the plug again inserted in the funnel, under which a 50 c.c. flask, previously weighed and warmed to prevent immediate solidification of the product, is then placed. The molasses is allowed to flow slowly into the flask until it reaches the base of the neck; in case the latter is soiled above the mark with the molasses it should be carefully cleaned with filter-paper.

The flask is then left for a time so that any air-bubbles still present may rise and is then cooled to 17·5° (or 20°) and weighed, the increase in weight giving the molasses taken. By means of a drawn-out pipette water is added carefully so that it does not mix with the molasses, the volume being thus made up to the mark. The amount of water added is determined either by subsequent weighing of the flask or by use of a graduated pipette. The volume of molasses is 50 c.c. less the volume of water, and since the weight of the molasses is known the specific gravity is easily calculated.

In many cases a result which is sufficiently exact is obtainable by the dilution method already described for dense juice (*q.v.*).

2. Water.—As well as by the direct or indirect method given for dense juice, the water in molasses may be determined as follows[1]:

Exactly 50 grams of the substance are weighed in a 400 c.c. conical flask, 200 c.c. of oil of turpentine being added and the liquid distilled from a sand-bath or oil-bath, a small condenser and a thermometer being used. The distillation begins at 90–95°, and the temperature then rises slowly to 155–160°; 130–150 c.c. of distillate are collected in a cylinder reading to 0·1 c.c., the volume of the aqueous layer being then read off; multiplication by two gives the percentage of water in the molasses.

3. Sugar.—Owing to the dark colour, only one-half the normal weight is dissolved to 100 c.c. Much froth being usually formed during the preparation of the solution, flasks with the neck widened above the mark are very useful in this case. When the substance is washed into the flask with a little water, it is clarified with basic lead acetate, this being added only so long as it continues to form a precipitate, so that large excess is avoided;

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[1] Testoni: *Staz. sper. agrarie italiane*, 1904, XXXVII, p. 366.

if the liquid remains highly coloured, it may be clarified further with a little fresh alumina cream. Sodium sulphate solution (some prefer sodium phosphate or a mixture of this with the sulphate) is next added to precipitate the excess of lead, the liquid being then mixed, made up to the mark, again mixed, left to stand for a time and filtered through a dry filter.

A preliminary test is made to ascertain if the molasses contains reducing sugar in sufficient amount to exert an appreciable influence on the polarisation. If this is not so, the polarisation, multiplied by two (or by four, if a 10 cm. tube is used) gives the percentage of saccharose.

In presence of invert sugar, 50 c.c. of the solution prepared as above are subjected to inversion in the usual way and polarised, the saccharose being calculated by Clerget's formula (see later: Raw Sugar).

Moreover, if raffinose is present, the inversion method is used and the result calculated as with raw sugar.

RAW SUGARS

These form more or less large yellowish-white to brown, moist crystals, with an unpleasant odour due to extraneous matters derived from the beet.[1]

Analysis always necessitates determinations of the sugar (saccharose) and of the soluble salts, since from these is calculated the yield (*rendement*) on refining. Determinations may also be made of the invert sugar, water, non-sugar and, in some cases, raffinose, total ash and alkalinity; sometimes sulphurous anhydride is tested for, but the colour is seldom measured.

Raw sugars are often non-uniform owing to the tendency of the syrupy liquid adherent to the crystals to collect at the bottom of the vessel. The whole sample should, therefore, be well mixed as rapidly as possible in a large porcelain dish with a spatula, all lumps being broken up; it is then returned to the vessel.

1. Determination of the Saccharose.—The polarisation gives the percentage of saccharose at once if other optically active substances are absent; the procedure is then as in (*a*). If, however, this is not the case, other active substances (invert sugar, raffinose) being present, method (*b*) [2] is followed.

In practice it is often the custom to give the polarisation rather than the true percentage of saccharose and to indicate separately the percentage of invert sugar.

(*a*) DETERMINATION OF SACCHAROSE IN ABSENCE OF OTHER SUGARS. In a tared German silver or nickel dish 26·048 grams (if vessels graduated according to Mohr at 17·5° C. are used) or 26 grams (if true c.c. at 20° C. are used) of the sugar are weighed, and are then washed through a funnel of the same material into a 100 c.c. flask. The dish and funnel are washed into the flask, which is filled to the extent of about three-fourths and shaken until solution of the sugar is complete; the liquid is then made up to the mark with water and mixed.

Usually the solution is coloured and turbid and requires clarification

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[1] Raw cane sugars have, however, pleasant odours.
[2] Invert sugar usually occurs in only small amount in raw beet sugars, but may be present to the extent of 2% or even more in cane sugars.

before polarising. For this purpose 50 c.c. are transferred to a 50–55 c.c. flask (the rest being retained for estimating the soluble ash) and basic lead acetate added drop by drop in just sufficient quantity to decolorise the liquid, 1–2 c.c. being usually required according to the depth of colour. To ascertain if the clarification is complete, the liquid is mixed and allowed to settle, and another drop of the basic lead acetate then added. The volume is made up to 55 c.c. with water, mixed and left for about 15 minutes to settle, the whole of the solution being then filtered through a dry filter about 12 cm. in diameter into a glass cylinder on a foot ; the funnel is kept covered to prevent evaporation. The first portion of the filtrate is some-times turbid and is then refiltered. In some cases clarification with the lead acetate is inadequate and it is then advisable, before the volume is made up to 55 c.c., to add a little alumina cream. Any froth formed may be expelled by a drop of ether. The polarisation is carried out in a 20 cm. tube, the result being increased by one-tenth to obtain the true percentage of saccharose.

(b) DETERMINATION OF SACCHAROSE IN PRESENCE OF OTHER SUGARS. The presence of invert sugar is detected by the preliminary test described below (see 2) or by means of Soldaini's solution. Raffinose is not usually found in sensible amount, but may be suspected in sugar obtained by work-ing up molasses. The presence of raffinose is indicated, although not always with certainty, by the elongated form of the crystals and by the relatively high polarisation, the sum of the latter and of the water and ash being about or even greater than 100.[1]

If only a small proportion of invert sugar is present, the true percentage of saccharose is obtained simply by adding to the polarisation 0·31 times the percentage of invert sugar.

When, however, the invert sugar exceeds 2%, or if raffinose is present, the *inversion method* must be used : The direct polarisation is determined as described above. Another quantity of 26·048 grams is then dissolved in about 80 c.c. of water in a 100 c.c. flask and basic lead acetate added, large excess being avoided. The solution is mixed, allowed to stand for a quarter of an hour and saturated sodium sulphate solution then added carefully and in just sufficient amount to precipitate the excess of lead ; it is then made up to volume, shaken, allowed to stand for a time, and filtered. Into another 100 c.c. flask are placed 50 c.c. of the filtrate, about 25 c.c. of water and 5 c.c. of hydrochloric acid (sp. gr. 1·188), inversion being then carried out in the ordinary way (see General methods, p. 114). The liquid is sub-sequently neutralised, made up to 100 c.c. and polarised at a temperature as near 20° as possible, the result being multiplied by two to allow for the dilution. From the polarisations before and after inversion saccharose is calculated, when invert sugar is present, by the Clerget formula [2] (see formula VIII, p. 117) :

$$X = \frac{100\,(P - P_1)}{142 \cdot 66 - 0 \cdot 5\,t},$$

[1] A very high polarisation accompanied by considerable reduction of Fehling's solution, indicates addition of starch sugar, but this is rare.

[2] The same formula serves in presence of added glucose.

or, when raffinose is present, by the formula (*see* p. 118):

$$X = \frac{0.5124\,P - P_1}{0.839},$$

in which P and P_1 are the polarisations before and after inversion, with their proper signs. In the rare instances of the simultaneous presence of invert sugar and raffinose (*see* General methods, p. 121), the last formula may be employed, but the polarisations must then be corrected for the invert sugar found.

2. Invert Sugar.—This is determined by one of the two methods indicated under (*b*) and (*c*). To ascertain if such determination is necessary, the preliminary test (*a*) is made.

(*a*) PRELIMINARY TEST. A solution of 5 grams of the substance in 20 c.c. of hot water is boiled in a flask with 12 c.c. of Fehling's solution for 2 minutes. If a red precipitate of cuprous oxide is formed in appreciable quantity, invert sugar is present. In such case, if the liquid has remained blue or if, after filtration and acidification with acetic acid, it gives a brownish-red precipitate or coloration with potassium ferrocyanide, it may be concluded that the invert sugar is small in amount or, at most, little more than 1%; method (*b*) is then used. If, however, the filtrate is colourless and gives no coloration with ferrocyanide, the invert sugar exceeds 1% and method (*c*) is employed.[1]

(*b*) HERZFELD'S METHOD. 25 grams of the sample are dissolved in water in a 100 c.c. flask, clarified with the necessary quantity of basic lead acetate, made up to volume and filtered. To 80 c.c. of the filtrate, transferred to another 100 c.c. flask, sodium phosphate or sulphate solution is added, drop by drop, until any excess of lead is precipitated; the solution is then made up to the mark, shaken, allowed to deposit and filtered. Of this filtrate 50 c.c., corresponding with 10 grams of the substance (in case clarification is unnecessary, 20 grams of the sample are dissolved to 100 c.c. and 50 c.c. of the filtered liquid taken), are used for the determination.

The 50 c.c. of sugar solution are mixed, in a conical flask of about 250 c.c. capacity, with 50 c.c. of Fehling's solution and heated rapidly to boiling, which is maintained for exactly 2 minutes; the subsequent procedure is as usual (*see* General methods, p. 109). The percentage of invert sugar is found by means of Table XVII. Since saccharose also reduces Fehling's solution slightly, a lower quantity of copper than 0.050 gram is regarded as indicating the absence of invert sugar or its presence in non-determinable amount.

(*c*) MEISSL AND HILLER'S METHOD. The clarified solution containing 20 grams of substance in 100 c.c. is prepared as in the previous method and a preliminary test made by running this solution, drop by drop, from a burette into a boiling mixture of 10 c.c. of Fehling's solution with 40 c.c. of water until the liquid is completely decolorised.

From the number of c.c. used, the quantity of invert sugar in the sugar

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[1] The preliminary test, repeated with suitable variation of the quantities of reagent and substance and taking into account the reducing power of invert sugar, may serve for the approximate determination of the latter.

solution is calculated approximately : 10 c.c. of Fehling's solution are decolorised by about 0·05 gram of invert sugar.

TABLE XVII

Percentage of Invert Sugar in Sugar, in Correspondence with the Amount of Copper weighed, using 10 grams of Substance (Herzfeld)

Copper. Mgrms.	Invert Sugar. %.	Copper. Mgrms.	Invert Sugar. %.	Copper. Mgrms.	Invert Sugar. %.	Copper. Mgrms.	Invert Sugar. %.
50	0·05	100	0·30	150	0·56	200	0·85
55	0·07	105	0·32	155	0·59	205	0·88
60	0·09	110	0·35	160	0·62	210	0·90
65	0·11	115	0·38	165	0·65	215	0·93
70	0·14	120	0·40	170	0·68	220	0·96
75	0·16	125	0·43	175	0·71	225	0·99
80	0·19	130	0·45	180	0·74	230	1·02
85	0·21	135	0·48	185	0·76	235	1·05
90	0·24	140	0·51	190	0·79	240	1·07
95	0·27	145	0·53	195	0·82	245	1·10

TABLE XVIII

Factors for the Calculation of Invert Sugar in Sugars containing more than 1% (Meissl and Hiller)

Ratio between Saccharose and Invert Sugar ($S : I$)	Approximate quantity of invert sugar in milligrams.						
	200	175	150	125	100	75	50
	Values of F						
0 : 100	56·4	55·4	54·5	53·8	53·2	53·0	53·0
10 : 90	56·3	55·3	54·4	53·8	53·2	52·9	52·9
20 : 80	56·2	55·2	54·3	53·7	53·2	52·7	52·7
30 : 70	56·1	55·1	54·2	53·7	53·2	52·6	52·6
40 : 60	55·9	55·0	54·1	53·6	53·1	52·5	52·4
50 : 50	55·7	54·9	54·0	53·5	53·1	52·3	52·2
60 : 40	55·6	54·7	53·8	53·2	52·8	52·1	51·9
70 : 30	55·5	54·5	53·5	52·9	52·5	51·9	51·6
80 : 20	55·4	54·3	53·3	52·7	52·2	51·7	51·3
90 : 10	54·6	53·6	53·1	52·6	52·1	51·6	51·2
91 : 9	54·1	53·6	52·6	52·1	51·6	51·2	50·7
92 : 8	53·6	53·1	52·1	51·6	51·2	50·7	50·3
93 : 7	53·6	53·1	52·1	51·2	50·7	50·3	49·8
94 : 6	53·1	52·6	51·6	50·7	50·3	49·8	48·9
95 : 5	52·6	52·1	51·2	50·3	49·4	48·9	48·5
96 : 4	52·1	51·2	50·7	49·8	48·9	47·7	46·9
97 : 3	50·7	50·3	49·8	48·9	47·7	46·2	45·1
98 : 2	49·9	48·9	48·5	47·3	45·8	43·3	40·0
99 : 1	47·7	47·3	46·5	45·1	43·3	41·2	38·1

The result of this test fixes the quantity of solution to be used in the determination—the amount of invert sugar present in any test should not exceed 0·2 gram.

The necessary quantity of the sugar solution is then mixed with 50 c.c. of Fehling's solution and the volume made up to 100 c.c. with water, the liquid being then boiled as in Herzfeld's method.

In the calculation use is made of the formula:

$$x = \frac{Cu}{p} \cdot F,$$

where x is the percentage of invert sugar, Cu the quantity of copper obtained, p the weight of substance used in the volume of solution taken for the test and F a factor varying with the quantities of invert sugar and saccharose in the solution and given in Table XVIII.

In order to make use of this table, it is necessary to know the *approximate* quantity of invert sugar in the solution used and the relation between the saccharose and invert sugar in the substance, referred to 100 of total sugars. The amount of invert sugar is approximately $Cu \div 2$.

The ratio between saccharose and invert sugar is calculated as follows: The percentage of invert sugar being approximately I, the percentage of saccharose, S, is calculated by adding 0·031 I to the polarisation of the product. The quantities of saccharose and of invert sugar in $(S + I)$ of total sugars being known, the quantities in 100 of total sugars are readily calculated. The factor F is then obtainable and hence the *exact* percentage of invert sugar in the substance analysed.

EXAMPLE: The Meissl method for determining invert sugar had to be used in the case of a sugar polarising 90·5. In the preliminary test about 5 c.c. of solution were required to decolorise 10 c.c. of Fehling's solution. The quantity to be used for the test should be less than 20 c.c. and, when 15 c.c. were used, 296 mgrms. of copper were obtained. The approximate amount of invert sugar is hence 296 ÷ 2 = 148 mgrms., so that the factor F must be taken from the column headed 150 mgrms.

Since 15 c.c. of solution contain 3 grams of substance, the approximate percentage I of invert sugar is

$$I = \frac{0·148 \times 100}{3} = 4·93,$$

and the percentage of saccharose will be

$$S = 90·5 + 0·31 \times 4·93 = 92·03$$

and the total sugars

$$S + I = 92·03 + 4·93 = 96·96.$$

The amounts of saccharose and invert sugar in 100 of total sugars will be

$$\frac{92·03 \times 100}{96·96} = 94·9$$

and

$$100 - 94·9 = 5·1,$$

so that the factor F must be taken from the line marked 95 : 5. The value of F is hence 51·2 and the percentage of invert sugar will be

$$x = \frac{0·296}{3} \times 51·2 = 5·05\%.$$

3. Raffinose.—The percentage of raffinose (anhydrous) is calculated by means of the formula (*see* p. 118) :

$$Y = \frac{P - X}{1 \cdot 852},$$

where P is the direct polarisation and X the percentage of saccharose calculated as indicated above (*see* above, 1, *b*).   If invert sugar also is present, the polarisation is corrected accordingly (*see* General methods, p. 121).

4. Soluble Ash (Soluble Salts).—20 c.c. of the solution of the normal weight in 100 c.c., prepared as in 1 (*a*) and filtered, are evaporated to a syrup in a tared platinum dish about 6 cm. in diameter, this usually requiring 3–4 hours.   The residue is treated with a few drops (about 0·5 c.c.) of concentrated sulphuric acid, the mass rapidly charring.   The carbonisation is completed by heating the dish on a sand-bath or carefully over a flame, care being taken to move the latter so as to prevent the porous, swollen mass from overflowing ; the residue is then incinerated in a muffle at a dull red heat, the temperature being kept below 700° so that the ash may not fuse.   Incineration is usually complete in an hour.

The sulphuric acid may be added to the solution before evaporation and in this case the evaporation on the water-bath should be continued until a semi-solid brown mass with a channelled surface is obtained.   This is heated on the sand-bath or over a flame until the charcoal becomes detached from the walls of the dish and is then incinerated as above.

The weight of the sulphated salts is diminished by one-tenth to obtain the weight of the non-sulphated salts (soluble ash) in the substance used ; this is calculated as a percentage by multiplication by 19·195 (for normal weight 26·048 grams) or 19·231 (for 26 grams).

5. Total Ash.—This differs from the soluble salts only when the sugar contains appreciable quantities of insoluble mineral impurities (sand, etc.). It is determined by weighing exactly 3 grams of the sugar in a platinum dish, adding about 0·5 c.c. of concentrated sulphuric acid and incinerating as described above.   The weight of the sulphated ash is diminished by one-tenth.

6. Water and Non-sugar.—An exact weight of 5–10 grams, according to the apparent amount of moisture present, is dried in a flat-bottomed metal (nickel or brass) or glass dish (furnished with a cover) in an oven regulated exactly at 105–110° for 2 hours or, with very moist products, longer.   The dish is allowed to cool in a desiccator and weighed, and then dried for a further period of half an hour to ensure the completion of the drying.

Subtraction of the sum of the percentages of water and sugar from 100 gives the *total non-sugar*, while further subtraction of the ash yields the *organic non-sugar*.

7. Calculation of the Yield on Refining (Rendement).—The rendement or yield of refined sugar obtainable is calculated on the assumption that certain extraneous or melassigenic substances hinder the crystallisation of the saccharose to extents which have been determined practically.   The extent to which the actual percentage of saccharose present is corrected

varies in different countries. In some cases, five times the percentage of soluble ash is subtracted; in others, the percentage of invert sugar, either as it stands or after multiplication by a factor, is also subtracted; in others again, four times the soluble ash and twice the reducing sugars are deducted, whilst sometimes fixed deductions are established for products of certain definite quality.

8. Alkalinity.—When the aqueous solution of the sugar has an alkaline reaction, the alkalinity of the sugar is determined by dissolving 20–50 grams in water and titrating the solution with N/10-sulphuric acid, as with defecated juice : the alkalinity is calculated as grams of CaO per 100 grams of sugar.

9. Detection of Sulphur Dioxide.—This test is made on sugars from juices decolorised by means of sulphurous acid. To a solution of 10–15 grams of the sugar in about 25 c.c. of water in a flask are added a scrap of pure zinc (or 0·3–0·4 gram of magnesium wire) and 5 c.c. of pure hydrochloric acid. In presence of sulphur dioxide, hydrogen sulphide is evolved and may be detected by the odour or by means of a strip of lead acetate paper.

10. Colour.—A definite quantity of the sugar (e.g., 20 grams) is dissolved in water to 100 c.c. and the colour determined as with dense juice and referred to 100 parts of pure sugar.

In practice, the sugar is sometimes merely compared with a series of types, such as the *Dutch standards*.

The importance of the determination of the depth of colour is diminished in consequence of the fact that raw sugars may be coloured with coal-tar colours. The latter may be tested for by extracting with alcohol or other solvent, fixing on wool and characterising by the methods given in the cases of macaroni, etc., or textiles.

REFINED SUGARS

Analysis of refined sugars is mostly reduced to the determination of the saccharose by direct polarisation. In some cases the ash and moisture are also determined, and in rare instances other determinations may be necessary, such as that of the reducing sugars (invert sugar and, perhaps, glucose or lactose added as adulterant) or raffinose; a test for saccharin is occasionally required.

The methods employed are those used for raw sugars (for glucose and lactose, *see* General methods ; for saccharin, *see* Liqueurs, p. 270). In general the solutions do not require clarification for the determination of the sugars, the solution of the normal weight being polarised as it is or after simple filtration.

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The refined sugars of commerce consist of almost pure saccharose and give polarisations differing little from 100 (99–100).

Raw sugars, especially colonial products, are also sold for direct consumption and these have far lower polarisations and may contain considerable proportions of invert sugar.

EXHAUSTED SLICES

These may be either fresh or dried. The former are prepared for analysis by reducing them to a pulp by means of the machines used for the non-exhausted slices; the latter are ground to a fine powder. As a rule only the sugar in these products is determined, but in some cases also the water.

1. Sugar.—Aqueous digestion in the hot is preferable (*see* Beet, 1, *b*). With moist slices, according to Pellet's method, double the normal weight is introduced with 1–2 c.c. of basic lead acetate into a 200 c.c. flask, 1·2 c.c. of water being added above the mark. On the other hand, according to Sachs and Le Docte's method, 60 grams of the pulp are taken with 177 c.c. of water containing basic lead acetate (a mean content of 89·7% of water being assumed, that is, 53·8 grams in 60 of the pulp). In either case the polarisation in a 20 cm. tube gives at once the percentage of sugar.

With dry slices, the half-normal weight is introduced with basic lead acetate into a 200 c.c. flask and the volume made up to 206 c.c.; or 12·64 grams of substance are made up to 200 Mohr c.c. or 12·62 grams up to 200 true c.c. The polarisation in a 20 cm. tube, multiplied by 4, gives the percentage of sugar.

2. Water.—This is determined by drying at 105–110° as with beet (*q.v.*).

WASTE AND WASH WATERS

In general, examination of these waters is limited to a qualitative investigation and possibly determination of the sugar. Sometimes also the dry matter may be required, this being determined either directly by drying or by measuring the specific gravity or saccharometric degree (*see* Diffusion Juice).

Sugar is detected in these waters by treating 2 c.c. of the liquid with 5 drops of 20% alcoholic α-naphthol solution and then carefully adding 10 c.c. of concentrated sulphuric acid (absolutely free from nitric acid) so that the two liquids do not mix. In presence of sugar, a violet ring forms at the surface of separation. A few comparative tests will indicate if the quantity of sugar is estimable; the reaction is very sensitive and detects even 0·001% of sugar.

When quantitative determination is necessary, the procedure is as with diffusion juice. With very small amounts of sugar, extra long polarimeter tubes are used, or the liquid is rendered faintly alkaline with a few drops of milk of lime and evaporated, the residue being neutralised with dilute acetic acid, clarified, made up to one-half or one-quarter of the original volume and polarised.

FILTER-PRESS SLUDGE

With these residues the only determination usually made is that of the sugar, which occurs partly in the free state and partly in combination with lime.

To determine the *free sugar*, 47 grams of the sludge, made into a paste

with a little water, are introduced completely into a 200 c.c. flask, the liquid being made up to the mark, shaken, filtered and polarised. The reading in a 20 cm. tube gives the percentage of free sugar directly, the difference between 47 grams and twice the normal weight compensating for the volume of the insoluble matter.

For the determination of the *total sugar*, 47 grams of the sludge are introduced, as before, into a 200 c.c. flask ; a few drops of phenolphthalein are added and then, drop by drop and with shaking, concentrated acetic acid, until the red coloration disappears. The liquid is next clarified with basic lead acetate solution, made up to the mark with water—the froth being dispelled with a drop of ether—shaken, filtered and polarised. The sugar combined with lime is equal to the total sugar less the free sugar.

Other Sugars

Besides saccharose, the principal sugar of commerce is glucose, which is dealt with in detail ; maltose syrup and invert sugar also occur and the analyses of these are considered briefly.

GLUCOSE

Commercial glucose, obtained by saccharification of starchy substances, is sold in the solid condition or in highly concentrated, syrupy solution ; the colour varies from white to brown. The samples for analysis should be taken in the manner already described for sugar or sugar syrups and should be stored in clean, dry, well-stoppered vessels.

The determinations usually made are those of water, ash, reducing sugars and dextrin ; it may sometimes be necessary to determine the insoluble matter, to test for artificial sweetening substances and, especially with syrups, to determine the acidity and sulphur dioxide.

1. Moisture.—An exact weight (2–3 grams) is introduced into a flat porcelain dish, tared together with a glass rod and about 50 grams of coarse siliceous sand, previously washed and ignited. If the glucose is solid or very syrupy, a little distilled water is added and the whole well mixed, evaporated to dryness on a water-bath, and dried in an oven at 105° to constant weight.

2. Ash.—From 5 to 10 grams are dried in a platinum dish on a sand-bath (if syrupy, first on a water-bath), the residue being cautiously charred over a small flame and then incinerated, best in a muffle.

If the amount of ash is large, it may be tested qualitatively, particularly for calcium sulphate and sodium chloride, which are derived from the process of manufacture.

3. Reducing Sugars.—Besides glucose, the commercial sugar contains also small quantities of other sugars, especially maltose and isomaltose. The exact determination of the separate sugars is not, however, easy owing to the presence of dextrin, the rotatory power of which is somewhat variable and not accurately known. It is usual, therefore, to calculate the whole of the reducing sugars as glucose.

The determination is made with Fehling's solution, either gravimetrically

or volumetrically. 10 grams of solid glucose or 15–20 grams of syrup are dissolved to 1 litre and the liquid filtered, if necessary, through a covered, dry filter.

For the gravimetric method, which is the more exact, 25 c.c. of this solution are used, the procedure already given being followed (*see* General methods, p. 109).

If the volumetric method is used, several flasks are charged each with 10 c.c. of Fehling's solution and 40 c.c. of water, the procedure given on p. 112 being followed. If a is the number of c.c. of the sugar solution required to decolorise the 10 c.c. of Fehling's solution and p the weight of the sugar taken per litre, the percentage of glucose in the sample will be $\dfrac{4945}{a.\ p}$.

4. Detection and Determination of Dextrin.—An indication of the presence of dextrin will be given by the polarisation, which will be considerably greater than that calculated for the glucose.[1]

The dextrin may be determined quantitatively with sufficient accuracy on the basis of the transformation of the various dextrins into glucose or inversion. One of the two following methods is used :

(*a*) A solution of 5 grams of the sugar in 400 c.c. of water is mixed with 40 c.c. of hydrochloric acid (sp. gr. 1·125) and the liquid heated in a reflux apparatus on a boiling water-bath for about 2 hours. It is then cooled, neutralised almost completely (to a faint acid reaction) with caustic soda and made up to 500 c.c., the glucose present being then determined as in 3 (above). The increase in the amount of glucose, multiplied by 0·9, gives the quantity of dextrin.

(*b*) A solution of 10 grams of the substance in a little water in a 100 c.c. flask is mixed with 20 c.c. of a hydrochloric acid solution of sodium chloride (200 grams of sodium chloride in 8oo c.c. of water and 200 c.c. of concentrated hydrochloric acid). The flask is immersed for an hour in boiling water and then cooled, the liquid being neutralised almost completely and made up to volume. The total glucose after inversion is then determined either by means of Fehling's solution as in (*a*) or approximately by means of the polarimeter ; in the latter case, the inverted solution, clarified, if necessary, with basic lead acetate, is read in a 20 cm. tube. The saccharimetric reading, multiplied by 10 and divided by 3·048, gives the percentage of glucose. The dextrin is then calculated, as in (*a*), from the glucose before and after inversion.

5. Insoluble Matter.—20 grams of the substance are dissolved in at least 300 c.c. of water, the solution being filtered through a filter previously dried at 105° and tared, and the insoluble residue thoroughly washed, dried at 105° and weighed. The residue is examined microscopically for starch.

6. Acidity.—This is expressed in c.c. of normal soda solution per 100 grams of substance and is determined by titrating a solution of 10 grams in water with N/10-soda, using sensitive litmus paper or phenolphthalein as indicator.

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[1] It should, however, be noted that maltose and isomaltose also have dextro-rotations greater than that of glucose.

7. Sulphur Dioxide.—This is determined as in wine or beer (*q.v.*).

8. Artificial Sweetening Substances.—These are detected in a moderately concentrated solution of the substance by the methods given for liqueurs (*see* Spirits and Liqueurs).

* * *

The purer commercial solid glucoses are white, odourless and compact, those of second quality being less compact and more or less yellow. Syrups of first quality should be colourless, odourless and clear, those of second quality being yellow but also clear, and inferior ones more or less brown. Turbidity in syrup is due to incomplete saccharification or to mineral matters or micro-organisms.

In general, solid glucoses contain 60–80% of glucose, 3–15% of dextrin and other unfermentable organic substances, 5–20% of water and 0·2–0·7% of ash. Very pure glucoses are also sold, these containing 90–96% or even more of glucose and only very small quantities of other organic substances.

Glucose syrups usually contain 30–55% of glucose, 30–50% of dextrin and the like, and 15–25% of water ; the ash is commonly 0·2–0·7, but may be as high as 2·5%. With unaltered syrups the acidity should not require for neutralisation more than 2 c.c. of N-soda per 100 grams, and it is sometimes required that the sulphur dioxide be not greater than 40 mgrms. per kilo, although a much larger quantity is often found.

MALTOSE

Maltose is put on the market in the solid form, and as syrup, which usually contains also other sugars (especially glucose) and dextrin. Of this type, too, are *malt extracts*, including those which are used industrially —owing to the enzymes (diastases) they contain—to render starch soluble, e.g., *Diamalt, Diastofor*, etc.

The analysis of maltose syrups is carried out similarly to that of glucose, determinations of the reducing sugars and dextrin being of particular importance. With malt extracts, a determination of the diastatic power may also be required.

1. Reducing Sugars.—The exact determination of the separate reducing substances in these products being a matter of great difficulty, they are usually determined together and the result expressed as either maltose or glucose.

The solution is prepared by dissolving 20 grams of the syrup in water, clarifying with basic lead acetate, removing the excess of lead with sodium sulphate and making up to 1 litre.

The reducing power of the filtrate towards Fehling's solution is measured either gravimetrically or volumetrically. In the former case the directions given for maltose (*see* General methods, p. 110) are followed and the calculation made in accordance with Table XIV on p. 111.

If, however, the volumetric method is used, the procedure already indicated (*see* General methods, p. 112) is followed, the duration of boiling being 4 minutes. The result is calculated either as maltose (coefficient, 0·741) or as glucose (coefficient, 0·4945).

2. Dextrin.—The glucose is determined after inversion of the dextrin,

as described for glucose (*q.v.*, 4), and from this is subtracted the percentage of pre-existing reducing sugars, determined as in 1 (above), expressed as maltose and multiplied by 1·053 (glucose resulting from the inversion of the maltose present). The remainder, multiplied by 0·9, gives the percentage of dextrin.

3. Diastatic Power.—This determination consists in a test of the saccharification of starch by means of the substance and may be carried out as follows [1] :

Starch paste is prepared by mixing 15 grams of arrowroot starch with 40 c.c. of cold water and pouring the paste into 400 c.c. of boiling water, the liquid being then kept in a boiling water-bath for half an hour with frequent stirring and subsequently allowed to cool and made up to 500 c.c. with water.

On the other hand, 2 grams of the substance are dissolved in 100 c.c. of water and determinations made of the *liquefying power*, that is, of the capacity of the substance to render starch soluble and of the true *diastatic power*, that is, of the capacity to saccharify starch.

(*a*) *Liquefying power*. To determine this, 165–170 c.c. of the starch paste (containing about 5 grams of starch) are introduced into a 200 c.c. flask, which is immersed in a bath at 40°. When a thermometer in the paste indicates the temperature 38–40°, a known volume of the 2% solution of the substance, usually 20 c.c. (corresponding with 0·4 gram of the substance), is added, the flask being shaken, returned to the bath and observed every half-minute. Liquefaction is regarded as attained when the liquid becomes mobile and when, after shaking, the air-bubbles rise rapidly to the surface. From the time thus taken for 0·4 gram of the substance to render soluble 5 grams of starch, the number of grams of starch which would be rendered soluble by 1 gram of the substance in 30 minutes is calculated, this number expressing the liquefying power.

(*b*) *Diastatic power*. The flask is then returned to the bath and kept for half an hour at 38–40°, 3 c.c. of 10% sodium hydroxide solution being then added and the liquid cooled rapidly and made up to 200 c.c. with water. In this solution the reducing sugars are determined volumetrically by means of Fehling's solution, each test being boiled for 4 minutes. The result is calculated as maltose in 200 c.c. of solution, i.e., per 0·4 gram of the substance, the maltose corresponding with 1000 grams of substance being calculated by proportion. Subtraction of the proportion of reducing sugars (expressed as maltose) pre-existent in the substance leaves a remainder which represents the quantity of maltose in grams formed in 30 minutes by the diastatic action of 1,000 grams of the substance, i.e., the diastatic power.

EXAMPLE : To render soluble 5 grams of starch by 0·4 gram of the substance required 2 minutes, the amount of starch made soluble by 1 gram of substance in 30 minutes being $\frac{5 \times 30 \times 1}{2 \times 0\cdot4} = 187\cdot5$ (liquefying power).

After half an hour's saccharification, titration with Fehling's solution indicated 2·144 grams of maltose per 200 c.c. of the solution, i.e., 5360 grams of

[1] *See* Pollak: *Ber. der VIth Intern. Kongress für angew. Chemie in Berlin,* 1903, Vol. III, p. 581.

maltose formed per 1000 grams of substance. The substance contained 45% of reducing sugars (as maltose), i.e., 450 grams in 1000 grams, so that the net weight of maltose formed in 30 minutes by the action of 1000 grams of the substance will be $5360 - 450 = 4910$ (diastatic power).

INVERT SUGAR

The analysis of invert sugar syrups usually consists in determining the reducing sugars by means of Fehling's solution either gravimetrically or volumetrically (see General methods), the result being expressed as invert sugar. Sometimes the saccharose is estimated, this being done by the inversion method.

Products containing Sugars

These include mainly crystallised fruits, preserved fruits, jams, chocolates, sweetmeats, biscuits, effervescent citrate of magnesia, honey, condensed milk, liqueurs and sweet wines. Certain of these products are dealt with in other places, condensed milk, liqueurs and sweet wines, for instance, in the chapters dealing respectively with milk, spirits and liqueurs, and wines. The others are treated below, special attention being paid to the determination of the sugars.

CRYSTALLISED AND CANDIED FRUITS

These are fruits impregnated and coated with sugar and are prepared by immersion and boiling in successive syrups of gradually increasing concentration. In some cases the amount and composition of the ash are determined, and tests made for injurious metals and for sweetening, antiseptic and colouring materials (see Preserves).

Determination of the Sugars.—The principal sugar present is saccharose, but invert sugar is also found—mostly due to inversion of the saccharose during the preparation of the fruits—as well as glucose, which is added directly. The method of determination is as follows :

(a) PREPARATION OF THE SOLUTIONS. A definite weight of the material, e.g. 40, 50 or 100 grams, is pounded in a mortar with hot water containing in suspension a little precipitated calcium carbonate to neutralise any free organic acids present. The paste is transferred quantitatively into a 200, 250 or 500 c.c. flask, according to the amount of the sample taken, the flask being filled to the extent of about three-fourths and left until the next day. Basic lead acetate is then added so long as it produces a precipitate, the liquid being well shaken and left at rest for some time, after which the excess of lead is precipitated with saturated sodium sulphate solution and the whole vigorously shaken for a while. After a further stand, the volume is made up with water, excess of the latter equal to 6% of the weight of the fruit taken for the determination being added to compensate for the volume of the insoluble matter ; after thorough mixing, the liquid is filtered through a dry filter.

50 c.c. of the filtrate are inverted in a 100 c.c. flask with 5 c.c. of hydro-

chloric acid (sp. gr. = 1·10), neutralised with sodium or potassium hydroxide, made up to 100 c.c. and, if necessary, filtered.

(b) DETERMINATION OF THE SACCHAROSE AND REDUCING SUGARS. The polarisations of the filtered non-inverted and inverted liquids are read on the Ventzke scale at a definite temperature, as nearly 20° C. as possible. The percentage s of saccharose in the substance analysed is then calculated by Clerget's formula :

$$s = \frac{26 \cdot 048 \, (P - P_1)}{142 \cdot 66 - 0 \cdot 5 \, t},$$

where P and P^1 are the polarisations—with the proper signs—before and after inversion, referred to 100 grams of substance in 100 c.c., and t the temperature of the liquid during the reading.

In both inverted and non-inverted solutions the reducing sugars are determined volumetrically by means of Fehling's solution (see General methods, p. 112). If n is the total dilution undergone by the non-inverted solution of g grams of the substance in V c.c. before the Fehling reduction and a the number of c.c. of solution used to reduce 10 c.c. of Fehling's solution (mixed with 40 c.c. of water), the percentage r of reducing sugars (calculated as invert sugar) originally present in the substance is given by :

$$r = \frac{5 \cdot 15 \, n \, V}{{}_t a \, g}.$$

Similarly the percentage r' of total reducing sugars after inversion is given by :

$$r' = \frac{5 \cdot 15 \, n' \, V}{a' \, g}.$$

The percentage of saccharose determined polarimetrically may be checked by the formula :

$$s = 0 \cdot 95 \, (r' - r).$$

To ascertain if the reducing sugars consist of invert sugar alone or if added glucose is also present, the rotation due to the total reducing sugars after inversion, regarding these as invert sugar, is calculated : 1 gram of invert sugar in 100 Mohr c.c. gives a deviation of $-1 \cdot 191$ Ventzke divisions at 20° C.

If such rotation is about equal to, or less lævo-rotatory than, that observed in the inverted liquid, only invert sugar is present. In such case, since the invert sugar originally present arises from the inversion of part of the saccharose used in the manufacture, the total quantity of saccharose added is equal to that actually found plus the amount of invert sugar multiplied by 0·95.

If, however, the calculated rotation is more lævo-rotatory than that observed, glucose also is present, the quantities of the separate sugars present being then determined as in (c).

(c) DETERMINATION OF THE SEPARATE SUGARS IN PRESENCE OF GLUCOSE. If the glucose used were pure and free from dextrin, the quantities of pre-existing invert sugar and glucose could be calculated as in general methods (p 118) or by means of the following formulæ :

$$x = \frac{P - a\,r - 3 \cdot 839\,s}{3 \cdot 048 - a},$$
$$y = r - x,$$

where x and y are the respective percentages of dextrose and invert sugar in the substance, a the Ventzke rotation of 1 gram of invert sugar in 100 c.c. in a 20 cm. tube at the temperature used ($- 1 \cdot 191$ at $20°$) and P, r and s have the same significations as in preceding formulæ.

Since, however, commercial glucose (usually liquid glucose) such as is used in making these products almost always contains marked proportions of dextrin, the above formulæ are inapplicable, unless indeed to give confirmation of the addition of glucose. The quantity of the latter is determinable only when the composition of the commercial glucose employed is known. When a sample of this glucose is available, it may be analysed with sufficient approximation as in (1), the results being then applied to the analysis of the crystallised fruit as in (2).

1. *Examination of the glucose.* A 100 c.c. flask containing 10 grams of the glucose, about 50 c.c. of water and 5 c.c. of hydrochloric acid of sp. gr. $1 \cdot 10$ is heated at $67–70°$ for a quarter of an hour as in the inversion of saccharose (to obtain the same conditions as in the analysis of the fruit), the liquid being then cooled, neutralised and made up to volume.

The solution thus obtained is read in the saccharimeter in a 20 cm. tube at about $20°$ C., while the reducing sugars are determined volumetrically with Fehling's solution and calculated as glucose (*see* Glucose, p. 141). Finally, the polarisation (referred to 100 grams of substance in 100 c.c.) is divided by the percentage of glucose found, the result being the so-called *polarisation coefficient* (c) of the commercial glucose, i.e., the saccharometric rotation in a 20 cm. tube of a solution containing in 100 c.c. such quantity of substance as contains exactly 1 gram of pure glucose.

2. *Examination of the crystallised fruit.* The polarisation and reducing power of the inverted solution, prepared as in (*a*) (*see* p. 145), are determined. As in (*b*) (*see* p. 146), P_1 is taken to be the polarisation after inversion and r' the percentage of reducing sugar after inversion, this being calculated, not with the coefficient $0 \cdot 515$ for invert sugar, but with a coefficient which lies between those for invert sugar and glucose and is usually placed equal to $0 \cdot 510$. If x and y are the percentages of *pure* glucose and of invert sugar :

$$x + y = r'$$
$$c\,x - 1 \cdot 191\,y = P_1,$$

so that :

$$y = \frac{c\,r' - P_1}{c + 1 \cdot 191}$$
$$x = r' - y.$$

From the percentage y of invert sugar, the total saccharose added is deduced by multiplying by $0 \cdot 95$, while the percentage of commercial glucose added is obtained by dividing $100\,x$ by the percentage of pure glucose in the commercial glucose.

EXAMPLES : 1. A solution of 40 grams of crystallised fruit in 200 c.c. gave the rotation, + 33 Ventzke divisions, at 20° C. in a 20 cm. tube, and the same solution after inversion (made up to double the original volume) gave the rotation − 6·7 ; thus $P = 33 \times 5 = + 165$ and $P_1 = - 6·7 \times 10 = - 67$. The reducing sugars, determined with Fehling's solution and calculated as invert sugar, were 1·98% before, and 49·22% after inversion. According to Clerget's formula, the saccharose is :

$$s = \frac{26·048 \ (165 + 67)}{132·66} = 45·55\%.$$

The results of Fehling titration give for the saccharose :

$$s = 0·95 \ (49·22 - 1·98) = 44·88\%,$$

which, given the complex nature of the product examined, agrees sufficiently well with the preceding result.

The calculated rotation for 49·22% of invert sugar is :

$$- 49·22 \times 1·191 = - 58·6,$$

and since the observed rotation after inversion is − 67 and hence more lævo-rotatory, excess of levulose and thus absence of added glucose is indicated. Indeed, the formula for the percentage of dextrose, namely :

$$x = \frac{+ 165 + 1·191 \times 1·98 - 3·839 \times 45·55}{3·048 + 1·191},$$

gives a negative result and therefore indicates absence of dextrose.

2. In the case of crystallised fruit containing glucose, a solution of 10 grams of the commercial glucose used in 100 c.c. gave a reading of + 57·2 Ventzke divisions in a 20 cm. tube at 20° C., the reading for 100 grams in 100 c.c. being hence + 572 ; titration with Fehling's solution gave 56% of reducing sugars (pure glucose), the polarisation coefficient thus being :

$$c = \frac{572}{56} = + 10·21.$$

The inverted solution obtained from the fruit (40 grams in 200 c.c. ; 50 c.c. of this inverted and made up to 100 c.c.) gave the reading + 32, so that $P_1 = + 320$; Fehling titration of the same inverted solution indicated 54·20% of total reducing sugars.

The two equations :

$$x + y = 54·20$$
$$10·21 \ x - 1·191 \ y = 320$$

give :

$$y = 20·47$$
$$x = 54·20 - 20·47 = 33·73.$$

From the percentage y of invert sugar, that of saccharose is found to be 20·47 × 0·95 = 19·45, while the percentage x of pure glucose shows that of commercial glucose to be $33·73 \times \dfrac{100}{56} = 60·23$. The crystallised fruit thus contains :

Saccharose added = 19·45%
Commercial glucose added = 60·23%

***

The value of crystallised fruits depends, besides on the quality of the fruit used and the method of preparation, essentially on the quantity of sugar and of glucose present. Genuine products should contain neither added antiseptics or artificial sweetening agents nor injurious metals,

PRESERVED FRUIT

This consists of fruit immersed in a sugar syrup prepared with saccharose, with or without glucose. Analysis of such products usually comprises the determinations made with crystallised fruit (*q.v.*), and a few hints may be given with reference to the determination of the sugars.

Determination of the Sugars.—The respective weights of fruit and of syrup taken must be proportional to those contained in the whole sample. The latter is weighed with the containing vessel and is then poured into a large funnel and allowed to drain completely into a flask. The vessel is weighed first empty and then after the fruit alone has been returned to it, the weights of syrup and fruit being thus obtained. A sample of 100 grams, containing the proper proportions of syrup and fruit, is reduced to a paste with hot water containing a little calcium carbonate in suspension, the subsequent procedure being exactly as with crystallised fruit ; the saccharose and the reducing sugars (invert sugar, glucose) are calculated per 100 of the total sample (fruit plus syrup).

To ascertain the quantity of sugar (saccharose) used in the preparation of the preserved fruit, from the total sugar (invert sugar $\times$ 0·95 plus saccharose) contained in the sample must be deducted the natural sugar (also calculated as saccharose) due to the quantity of fruit in the sample. For this purpose it is, of course, necessary to know the saccharine contents of different fruits, so that an analysis of fruit of the same quality preserved in water in the same conditions as in the syrup must be made.

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As regards the deductions to be drawn from the analytical results, what was said concerning crystallised fruit applies also in this case.

JAMS

Jams or *fruit preserves* result from the boiling of fruit pulp with saccharose and often with glucose as well. Similar products are *fruit jellies* obtained from fruit juice instead of pulp and *fruit syrups*, made by mixing fruit juice with sugar syrup without boiling. With such materials the following determinations and tests are made.

1. Determination of the Sugars.—A mixture of 50 grams of the substance with hot water containing calcium carbonate is treated exactly as indicated for crystallised fruit.

2. Insoluble Substances.—These are determined particularly in the case of jams. 25 grams of the substance are heated with about 150 c.c. of water for half an hour on a water-bath with frequent stirring, the liquid being decanted on to a filter dried at 105° and tared and the residue washed with boiling water and ultimately transferred to the filter. If necessary, filtration is aided by slight suction. The filter with the insoluble residue is dried at 105° and weighed, the filtrate being made up to a known volume (e.g., 250 c.c.) and kept for other determinations.

3. Extract.—20 c.c. of the above filtrate are evaporated to dryness

in a platinum dish and the residue dried at 100-105° to constant weight.

The extract may also be determined indirectly with sufficient accuracy by determining the specific gravity of the solution and deducing the percentage of dissolved matter (calculated as saccharose) by means of tables (e.g. that used for calculating the extract of wines : *see* later) or by means of a saccharometer.

The dry extract, less the sugars (saccharose plus reducing sugars) gives the *non-saccharine extractives* (dextrin, etc.).

4. Water.—This may be determined either directly as in dense juices and syrups (p. 130) or indirectly by subtracting from 100 the percentages of insoluble matters and extract.

5. Ash.—From 5 to 10 grams are dried in a platinum dish, and the residue cautiously charred over a flame and incinerated in a muffle at a dull red heat.

If the ash is large in amount, it may be tested qualitatively for the detection of mineral substances present (barium sulphate, gypsum, chalk, sand, etc.) and of heavy metals.

6. Injurious Metals.—These may be derived either from the vessels in which the products are prepared or stored or from mineral colours added ; to some extent they may be detected in the ash. For a more complete investigation, especially of metals which may be eliminated during the incineration as volatile compounds, use is made of one of the known methods for the destruction of organic substances, e.g., treatment with hydrochloric acid and potassium chlorate, the residue being examined by the ordinary methods of qualitative analysis.

7. Acidity.—If volatile acids are not present, this determination is made on the solution obtained as in 2 (above), a known volume being titrated with N/10-alkali in presence of phenolphthalein and the result expressed in c.c. of N-alkali per 100 grams of substance.

In presence of appreciable amounts of volatile acids, a separate weighed portion of the substance is mixed with cold water to a definite volume and an aliquot part of the liquid decanted or, if necessary, filtered through glass wool, and titrated as above (*total acidity*). The *fixed acidity* is determined by evaporating almost to dryness on a water-bath a known volume of the solution obtained as in 2 (above), the residue being taken up in water and titrated as before ; *volatile acidity* = total acidity minus fixed acidity.

8. Extraneous Organic Colouring Matters.—Tests are made especially for artificial organic colouring matters by the methods indicated for liqueurs and wines (*q.v.*).

9. Antiseptics.—These—particularly sulphurous, boric and salicylic acids and formaldehyde—are tested for as in wine and beer (*q.v.*).

10. Artificial Sweetening Agents.—As in liqueurs (*q.v.*).

11. Detection and Determination of Dextrin.—Dextrin occurs especially in products containing commercial glucose and its presence is demonstrated by the high dextro-rotation (*see* Crystallised Fruit, Determination of the Sugars, *c*). To determine it, 100 c.c. of the inverted solution, prepared as for the determination of the sugars (*see* 1), are treated as indicated on p. 142 (section 4) to transform the dextrin into glucose,

the reducing sugars in the resultant liquid being determined with Fehling's solution. The difference between the reducing sugars thus found and those found in the inverted solution, multiplied by 0·9, gives the amount of dextrin.

12. Gelatine.—From 20 to 30 grams of the substance are dissolved in about 10 c.c. of water in a porcelain dish and precipitated with 100–150 c.c. of alcohol, the mass being allowed to stand, the liquid decanted off, and the precipitate remaining adherent to the dish divided into two parts. One of these is heated in a test-tube with quicklime : in presence of gelaine, ammonia is evolved. The other is dissolved in water and the solution tested with picric acid or tannin solution, which gives a precipitate in presence of gelatine.

13. Gelose (Agar-agar).—This usually contains diatoms, which may be separated and recognised microscopically. For this purpose, the substance is boiled with 5% sulphuric acid containing a few crystals of permanganate, the insoluble part being allowed to settle and observed under the microscope ; another method consists in centrifuging the substance after heating with a little hydrochloric acid and examining the deposit. The diatoms peculiar to gelose are recognised by their characteristic appearance : in particular, *Arachnoidiscus japonicus*, which is circular with its surface marked by pronounced radial striæ.

Certain qualities of very pure gelose, which do not contain diatoms, may be detected as follows : Precipitation with alcohol is carried out as in the test for gelatine, the precipitate obtained being dissolved in 50 c.c. of boiling water and the solution treated with lime water until distinctly alkaline, and boiled for 2–3 minutes and filtered through linen. The filtrate is neutralised almost completely by oxalic acid solution and evaporated to dryness on a water-bath, the residue being broken up with a glass rod. If gelatine is present, the mass is treated with 2 c.c. of formaldehyde and again evaporated to dryness. In either case, the residue is taken up in 50 c.c. of water and the liquid boiled for some minutes and filtered hot through a hot water or steam funnel. The filtrate is evaporated to 6–8 c.c. and poured into a test-tube : if gelose is present, the liquid sets to a gelatinous mass on cooling.

14. Microscopic Test.—This is carried out more especially with jams and preferably in comparison with samples of certain origin, in order to characterise the particular tissues of the fruit used and to detect any elements of different fruits, which may be present particularly in products prepared with residues from the manufacture of crystallised fruit.

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Jams and jellies contain marked proportions of sugars (usually 50–70%, including the dextrin of any glucose used), which constitute almost the whole of the dry extract in jellies, whilst jams usually contain appreciable quantities of non-saccharine extractives (up to 5–6% or more). The amount of insoluble matter is appreciable in jams but negligible in jellies. In genuine products the ash usually varies from 0·2 to 0·4%, and the acidity varies with the nature of the fruit, but in unaltered products it should as a rule be neutralised by a few c.c. of N-alkali per 100 grams and should result wholly from fixed acids.

Genuine products should not contain extraneous colouring matters, antiseptics, artificial sweetening agents or injurious metals and should not be treated with gelatine or gelose.

CHOCOLATE

Pure chocolate is a mixture of torrefied, powdered cacao with sugar (saccharose) ; sometimes excess of fat is added and sometimes a small quantity of various essences or spices. *Starch chocolate* contains, in addition, one of a number of starches or flours (of rice, oats, chestnut, or of oily seeds such as walnut, arachis, etc.). Chocolate of lower quality sometimes contains powder cacao husks, and occasionally other sugars than saccharose (glucose) are added ; other adulterants are dextrin, gum and gelatine. *Milk chocolate* is prepared with cacao, sugar and milk powder or extract.

The analysis of chocolate comprises mainly the tests and determinations indicated below. With chocolates containing inclusions of extraneous substances (whole walnuts, almonds, etc., or liqueurs), it is advisable to separate mechanically the outer layer of chocolate from the included substance and to examine it separately.[1]

1. External Characters.—Note is made especially of the colour, consistency, homogeneity, odour and taste of the product ; with practice, useful conclusions with regard to the quality can then be drawn.

2. Microscopic Examination.—A few grams of the chocolate are freed from fat by extraction with carbon tetrachloride and from sugar by washing on a filter with a little alcohol and then with cold water. The residue, well mixed in a mortar, is examined with a magnification of 300–400 diameters, best in comparison with products of known origin. Such examination will show if the normal constituents of pure chocolate are accompanied by starch or flour of cereals, chestnuts (*see* Fig. 32 of Plate IV in the chapter on Flour) or oily seeds, or powdered cacao husks.

3. Water.—5 grams of the powdered chocolate are weighed in a flat porcelain dish, tared with about 20 grams of coarse siliceous sand previously washed and calcined and a glass rod ; the whole is thoroughly mixed and then dried at 100–105° for 5–6 hours.

4. Ash.—5 grams of the substance, weighed in a platinum dish, are carefully charred over a small flame and then incinerated in a muffle at a dull red heat. If any large amount of ash is left, it should be examined for added mineral matter and injurious metals.

5. Fatty Matter.—10 grams of the powdered chocolate are placed in a filter-paper thimble and extracted [2] with light petroleum ether or neutral carbon tetrachloride (the latter, however, dissolves also the caffeine).

To ascertain if the fat extracted consists entirely of cacao butter, its various constants may be determined (*see* Fatty Substances, Vol. I). As a

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[1] It may happen, especially in liqueur chocolates, that such separation is not possible. In such case the whole sample is reduced to a homogeneous mass and analysed, the alcohol also being determined by distillation after dilution. The water is then represented by the difference between the loss on drying and the alcohol (by weight) found.

[2] The Marino extractor is especially suitable for this operation.

rule the melting point and the Zeiss butyro-refractometer reading at 40° are sufficient, but in doubtful cases the saponification, iodine and Reichert-Meissl numbers, etc., may be measured.

6. Sugars.—In most cases only saccharose is found in chocolate; invert sugar, when present, is of negligible amount. In rare cases added glucose may be present, and in milk chocolate lactose occurs.

(a) When *saccharose alone* is present, 13·024 grams of the powdered chocolate are placed in a 100 c.c. flask and the same weight in a 200 c.c. flask, each quantity being moistened with alcohol, treated with 75 c.c. of cold water and frequently shaken during a period of about 45 minutes. After clarifying, if necessary, with basic lead acetate and alumina cream, each solution is made up to volume, filtered through a dry filter and polarised.

For the calculation it is necessary to know the volume v of the insoluble matter contained in the half-normal weight, this being given by the formula:

$$v = \frac{100 \ (a - 2 \ b)}{a - b},$$

where a and b are the respective polarisations of the solutions in the 100 and 200 c.c. flasks. The true polarisation of the half-normal weight dissolved in 100 c.c. will then be:

$$P = \frac{a \ (100 - v)}{100}.$$

The percentage of saccharose is equal to $2 \ P$.

(b) When *glucose and possibly invert sugar* are present, the volume of the insoluble matter is determined as in (a) and the analysis then carried out as described for other saccharine products (*see* Crystallised Fruit). The solution is prepared with the precautions indicated in (a), a volume of water being added above the mark equal to that of the insoluble matter contained in the weight of substance used. The saccharose is determined by the Clerget method and the reducing sugars by means of Fehling's solution, a sample of the glucose used in the manufacture being examined when necessary.

(c) In milk chocolate, the *saccharose* and *lactose* are determined by the methods given for condensed milk (*see* p. 33), allowance being made for the volume of the insoluble matters determined as in (a).

7. Dextrin.—When it is necessary to determine this, the method indicated for flours (p. 63) is applied to the defatted and dried substance (the residue from the extraction of the fatty matters, dried at 100°, may be used, but the results are referred to the substance itself).

The difference between the reducing sugars found after inversion of the dextrin and those found in the determination of the sugars after inversion of the saccharose is multiplied by 0·9 to obtain the amount of dextrin.

8. Starch.—The inversion method described for flour (p. 63) is employed. From 5 to 10 grams of the substance are freed from fat by extraction with petroleum ether or other suitable solvent and from sugars (and dextrins) by treatment with 25% alcohol. The glucose found, multiplied by 0·9, gives the quantity of starch.

With chocolate to which starch or flour has been added, since only a small part (usually 1–2%) of the starch present consists of that contained in the cacao, the quantity of the starch or flour added may often be determined sufficiently approximately from the starch content. When ordinary starch is added, it may be assumed that this contains on the average about 80% of actual starch, the rest being mostly moisture.

Where chestnut flour has been added, its composition may be taken as : moisture, 7–11% (in torrefied flour, 5–6%) ; saccharose, 23–31% (mean about 28%) ; reducing sugars, 1–2% ; starch, 36–41% (mean about 39%).[1] When a sample of the chestnut flour actually used is not available, a mean content of 39% of starch may be assumed, so that the extent of the addition is calculable from the proportion of starch found in the chocolate. The amount of saccharose corresponding with such amount of chestnut flour is then calculated and this value subtracted from the total saccharose found in the chocolate ; the remainder represents the saccharose actually added in the preparation.

9. Alkaloids.—These rarely occur in chocolate but, when necessary they may be determined as follows (Savini) : 12 grams of the powdered chocolate are introduced into a ½-litre flask and boiled with 70 c.c. of light petroleum on a water-bath for 15 minutes ; the solvent is then decanted on to a small filter and the operation repeated twice.

The flask with the defatted substance and also the filter are dried for a few minutes in an oven to expel the solvent, the filter being then introduced into the flask, together with 5 c.c. of 10% sulphuric acid and 250 c.c. of water. The liquid is boiled under a reflux condenser for an hour and then transferred while hot into a 300 c.c. measuring flask ; the original flask is rinsed out with hot water, but the filter-paper is not allowed to enter the measuring flask. After cooling to about 30°, the liquid is made up to volume and filtered, 250 c.c. of the filtrate (10 grams of substance) being evaporated in a porcelain dish containing 10 grams of fine sand with addition of a little magnesia to render the liquid alkaline.

The evaporation is continued until a syrup is obtained (as in the determination of glycerine in wine), sufficient magnesia (8–10 grams) being then added to give a dry powdery substance easy to detach with a spatula and to powder with a pestle.

The dry substance thus obtained is placed in a flask with 100 c.c. of chloroform, the spatula, pestle and dish being washed twice with 5 c.c. of hot water, which is added to the chloroform. After addition of 0·25 c.c. of concentrated ammonia, the liquid is boiled for 15 minutes under a reflux condenser. The boiling chloroform is filtered through a pleated filter, care being taken that the substance does not fall on to the filter. The residue in the flask is similarly treated with four further quantities of 100 c.c. of chloroform, the whole of the latter being then distilled to dryness from a flask on the water-bath and the last traces expelled in the oven. The residue is then washed with a little petroleum ether (10 c.c. in all, in two quantities), which is decanted on to a small filter.

The residue is next dissolved in a little boiling water and the solution filtered through the filter previously used, into a tared platinum dish, the flask being washed three times with a little boiling water. The liquid is

¹ G. Savini : *Annali di Chim. Applciata*, VI, 1916.

evaporated to dryness on a water-bath and the residue dried for an hour in an oven at 100° and weighed; the weight obtained, multiplied by 10, gives the percentage of alkaloids (theobromine and a little caffeine) contained in the chocolate.

10. Gelatine.—5 grams of the powdered chocolate are treated with 50 c.c. of boiling water, 5 c.c. of 10% lead acetate solution being then added and the liquid filtered. The filtrate is tested with a few drops of saturated aqueous picric acid solution : in presence of gelatine, a yellow precipitate forms.

11. Cacao and Added Fat.—The amount of cacao (without fat) used in the preparation of chocolate is best calculated, when possible, by difference. From the result thus obtained, if the fat present is really cacao butter, the natural cacao and the fat added are calculated on the assumption that natural cacao contains an average of 50% of fat. In the different cases the procedure is as follows :

(a) With *pure chocolate*, deduction from 100 of the sum of the water, sugar and fat gives the percentage of cacao without fat and this, multiplied by two, the natural cacao present ; the percentage of fat found, less that proper to the cacao, gives the added fat.

(b) With *chocolate mixed with starch*, the fat-free cacao is obtained by subtracting from 100 the sum of the water, sugar, fat and starch, the natural cacao and the added fat being then calculated as in the preceding case.

(c) In *chocolate with chestnut flour*, the mean composition of this flour is assumed (or a sample of the flour actually used is analysed). If the sum of the water, added saccharose, fat and chestnut flour is subtracted from 100, the remainder will represent approximately the percentage of cacao without fat ; the subsequent procedure is as before.

(d) With *milk chocolate* containing no other extraneous substances, the percentage of casein may be taken as approximately equal to that of the lactose found and the cacao and added fat hence calculated by difference. The fat-free cacao is deduced by subtracting from 100, the sum of the water, sugar, fat and twice the lactose ; the calculation of the natural cacao and added fat is then carried out as in the preceding cases.

(e) In more complex cases, such as that of *chocolate containing flour from oily seeds*, or of adulteration with various extraneous substances, it is not always possible to arrive at the cacao by difference. This may, however, sometimes be done when the composition of the flour from the oily seeds is known, the quantity of extraneous fat being calculated from the constants of the fatty substance. When this is not possible, the proportion of cacao may be calculated, although with only rough approximation, from the percentage of alkaloids found, decorticated natural cacao containing on the average 1·5% of these bodies. The result thus obtained must be very uncertain, since the variation in the alkaloid content is fairly wide.

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Pure chocolate usually contains from one-half to two-thirds of sugar and from one-half to one-third of cacao ; a slight excess of cacao butter is sometimes

added to render easier the formation of paste. When starch or flour is present, the amount of this varies considerably and may be as much as 40% or even more. Good chocolate should not contain more than 3% of moisture and 2·5% of ash, and should not be mixed with powdered cacao husk, glucose, fats other than cacao butter, dextrin, gelatine, or mineral matter.

SWEETMEATS

The analysis of sweetmeats is usually limited to a determination of the sugar, which is the principal constituent. Sometimes, however, it is necessary to test for and determine the starch and extraneous mineral matters and to test for colouring substances and artificial sweetening agents, the methods already indicated for other sugar products being employed.

Determination of the Sugar.—As a rule sweets contain no large proportion of insoluble matter, so that the saccharose is determined by dissolving 26·048 grams of the powdered sample to 100 c.c.—with addition of basic lead acetate if necessary—and filtering and polarising the solution. If a qualitative test with Fehling's solution shows the presence of reducing sugars, these are determined by the methods already described.

Where sweets rich in insoluble substances, such as starch, almonds, etc., are to be examined, the volume of the insoluble matter is determined as in the case of chocolates, i.e., by making two solutions of the normal weight in 100 and 200 c.c. respectively.

With sweets containing included extraneous matters (whole seeds, liqueurs, etc.), it is sometimes convenient to separate these mechanically and examine the external part separately.

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The value of sweets depends essentially on the content of sugar, but the absence of injurious substances must be ascertained.

JUJUBES

To determine the sugars in jujubes and other gummy saccharine products, the solution is prepared as follows (Savini) : 20 grams of the substance are dissolved in about 100 c.c. of hot water in a 200 c.c. flask, and on cooling, a mixture of 10 c.c. of basic lead acetate and 70 c.c. of 95% alcohol is added gradually and with shaking. After a rest of about an hour at the ordinary temperature, the volume is made up with water (allowing, where necessary, for the volume of the insoluble matter) and the solution filtered. 100 c.c. of the filtrate are neutralised with a few drops of acetic acid and evaporated on a boiling water-bath to expel the greater part of the alcohol. The residue is restored to a 100 c.c. flask, a little burnt alum being added to eliminate the excess of lead and the liquid made up to volume and filtered.

The filtrate is used for the determination of the sugars by the ordinary methods (*see* Crystallised Fruits). If saccharose alone is present the polarisation is, of course, sufficient.

BISCUITS AND MILK FLOUR

Biscuits consist essentially of flour and sugar, sometimes with the addition of fats (butter, etc.) and eggs. *Milk flour* contains, besides flour and sugar, also the constituents of milk, but products sold under this name are often quite free from any of the elements of milk.

In the case of biscuits, the sample for analysis should be prepared by taking the different kinds present in the proper proportions, powdering and mixing them thoroughly. The following determinations are made:

1. Microscopic Examination.—This is made with a view to ascertaining the nature of the flour (*q.v.*) used.

2. Water.—10 grams of the powdered substance are heated in a platinum dish at 105° to constant weight.

3. Ash.—The dried substance from the preceding determination is carefully charred over a small flame and then incinerated in a muffle at a dull red heat.

4. Fats.—These are determined by extraction with a suitable solvent, e.g., ether or carbon tetrachloride (*see* Chocolate). The necessary constants of the fat are then determined and its character established.

5. Sugars.—In most cases biscuits contain only saccharose, reducing sugars being in negligible amount, but invert sugar and glucose are sometimes found. In true milk flour, lactose is present in addition to saccharose. In the various instances the procedures are as follows:

(*a*) When *saccharose alone* is present, 40 grams of the powdered sample are mixed to a paste with a little water, the whole being then introduced into a 200 c.c. flask and water added to within a few c.c. of the mark. The mass is frequently mixed during some hours and then clarified with lead acetate and a little alumina cream, the lead being precipitated with sodium sulphate and the liquid made up to volume, shaken, filtered and polarised.

Since in this case the volume of the insoluble substances is considerable, it must be taken into account as indicated for chocolate, two solutions being prepared of different concentrations—one with 20 and the other with 40 grams of the substance to 200 c.c.—and polarising both.

When several samples of the same type are to be analysed, the trouble of preparing the two solutions may be avoided by determining once for all the volume of the insoluble substances in the various types of biscuit and hence the volumes of water which must be added above the mark in the different cases. For varying proportions of saccharose, experiment gives the following mean volumes of water to be added for 10 grams of biscuits taken:

About 20% of sugar, 5 c.c. of water to be added.

,,	30	,,	,,	4·5	,,	,,
,,	40	,,	,,	3·75	,,	,,
,,	50	,,	,,	2·25	,,	,,
,,	75	,,	,,	1·75	,,	,,

(*b*) In presence of *invert sugar* or *glucose*, the volume of the insoluble matter is determined as in (*a*) and the solution prepared with the necessary

addition of water beyond the mark, the subsequent procedure being as with crystallised fruits.

(c) In presence of *lactose*, the solution is prepared as above and the analysis carried out as with condensed milk (*see* this volume, p. 33).

6. Dextrin and Starch.—These are determined as in chocolate.

7. Nitrogenous Matter.—This is determined as in flour by the Kjeldahl method.

8. Artificial Sweetening Substances and Colouring Matters.—When necessary, these are tested for by the methods given for wine, spirits, etc. (*q.v.*).

* * *

The composition of biscuits is very variable, as regards both the sugar content and the presence, quantity and quality of fat. Genuine milk flour contains 20–60% of sugar (usually about 40%) and 4% of fat (butter), besides lactose and casein.

MARZIPAN

This consists essentially of sugar and almond paste. Besides the determination of the sugars, which is made as in biscuits, and the microscopic examination for the detection of other seeds and extraneous flours, tests for hydrocyanic acid (from the bitter almonds) and nitrobenzene (added as an adulterant) are also necessary.

1. Test for Hydrocyanic Acid.—25 grams of the substance are digested for an hour with 30 c.c. of water and a few drops of potassium hydroxide solution, the liquid being then rendered acid with sulphuric acid and distilled, the first 3 c.c. of distillate being collected and tested by means of the Prussian blue reaction, which is carried out as follows :

The liquid is made alkaline with potassium hydroxide and heated to boiling with a few drops of ferrous sulphate solution. A little ferric chloride is next added to the liquid, which is cooled and acidified with hydrochloric acid : in presence of hydrocyanic acid a blue precipitate is obtained or a greenish-blue liquid which deposits blue flocks on standing.

2. Test for Nitrobenzene.—About 25 grams of the substance are digested for some hours with 30 c.c. of cold alcohol, the mass being then filtered, and the filtrate diluted with an equal volume of water and heated on a water-bath with a little zinc dust and about 3 grams of caustic potash until the bulk of the alcohol is expelled. The residual aqueous liquid is decanted off and extracted with an equal volume of ether, the ethereal layer being separated and evaporated and the residue dissolved in 3 c.c. of water. This solution is heated with a few drops of chloroform and alcoholic potassium hydroxide solution : in presence of aniline, derived from nitrobenzene in the marzipan, the characteristic odour of phenylcarbylamine is emitted.

CITRATE OF MAGNESIA

So-called *effervescing citrates of magnesia* are mixtures consisting principally of sugar, tartaric acid and sodium bicarbonate ; in some cases glucose also is present.

The sugars in these products are determined as follows :

In a 200 c.c. measuring flask 40 grams (or 25–30 grams, if the sample is small) of the citrate are treated with about 100–120 c.c. of distilled water, gradually and with shaking so as to avoid too brisk an effervescence. When the substance is completely dissolved, a few drops of alcoholic phenolphthalein solution are added and then enough concentrated sodium hydroxide solution (not potassium hydroxide) to give a red coloration ; dilute acetic acid is then added drop by drop until the liquid is decolorised. The solution is then heated for half an hour on a boiling water-bath with 20 c.c. (or 15 c.c. when only 25–30 grams of the citrate are taken) of a 50% solution of crystallised calcium chloride to cause thorough deposition of the precipitated calcium tartrate. If then further addition of calcium chloride produces more precipitate, sufficient is added for complete precipitation and the flask left for about 12 hours in a cold place. The volume is then made up with water, 6 c.c. (or 4 c.c. for 25–30 grams of the citrate) of the latter being added in excess to make up for the volume occupied by the precipitate ; the whole is then thoroughly mixed and filtered through a dry, covered filter.

Two separate portions of 50 c.c. of the filtrate are placed in 100 c.c. flasks, one being made up to volume with distilled water and the other inverted in the ordinary way, neutralised and made up to volume ; both solutions are then polarised and the saccharose calculated by Clerget's formula. The results may be checked by volumetric determinations with Fehling's solution, the saccharose and the pre-existing reducing sugars being then calculated.

HONEY

Natural honey from bees consists of a highly concentrated aqueous solution of sugars (invert sugar—usually with predominance of levulose—and saccharose) and of small quantities of gummy and dextrinous matters, proteins, enzymes, wax, organic acids, esters and mineral substances. It is very often adulterated, mostly by addition of invert sugar, glucose and dextrin. *Artificial honey* is also sold, this consisting usually of commercial invert sugar mixed with aromatic substances or with natural honey.

Honey is analysed to ascertain if it is genuine or artificial or if any adulteration has taken place. To this end the following tests are made :

Sampling.—At least 250 grams of honey are required and this should be stored in a glass vessel with a ground stopper. The sample must first be thoroughly mixed, especially if there is even incipient separation into an upper liquid portion, mainly of levulose, and a lower minutely crystalline portion of dextrose. If the sample is to be taken from a large vessel, the whole of the contents should be carefully mixed and small amounts taken from different points in the bulk and thoroughly mixed.

1. External Characters.—Honey may be white (centrifuged honey) or brown (coniferous honey), or pale yellow, yellow, dark yellow, greenish yellow or reddish, and its taste should be more or less markedly sweet with an almost imperceptible bitter sensation (due to small proportions of malic

and formic acids). The aroma should be pleasant and that of normal honeys ; it often indicates the origin, the aroma of the flowers of fruit trees, acacia, rose or conifers, especially the last, being often recognisable.

2. Microscopic Examination.—50 grams of the honey are dissolved in about 150 c.c. of hot water and the solution filtered through a dry filter into a 250 c.c. flask. The filter is washed with small quantities of hot water and the solution made up to volume when cold and shaken ; this is used for tests 4, 6 and 9. The residue on the filter is usually small in amount and is examined microscopically under low and high powers to ascertain if pollen, starch granules, residues of the different organs of the bee, vegetable elements, etc., are present.

3. Determination of the Water and Dry Matter.—About 2 grams of the honey are weighed in a flat porcelain dish together with a glass rod and 10–20 grams of washed and calcined sand. The mass is well mixed with addition of 5 c.c. of distilled water and the dish then placed on a boiling water-bath ; the mixing is continued and when it becomes difficult, the dish is dried in a steam-oven to constant weight, the weighing being carried out rapidly. The loss represents water and is calculated as a percentage. Deduction of the latter from 100 gives the *dry matter* and this, less the total sugars (*see* below), the *dry matter other than sugar*.

4. Acidity.—50 c.c. of the solution prepared as in 2 (above) are titrated with N/10-KOH until a drop of the liquid no longer reddens blue litmus paper. The acidity is expressed usually in c.c. of N-KOH per 100 grams of honey, but sometimes as formic acid : 1 c.c. N/10-alkali = 0·0046 gram of formic acid.

5. Ash and its Alkalinity.—About 10 grams of the honey are carefully charred in a platinum dish over a small flame and then incinerated in a muffle. The alkalinity of the ash is determined by heating the latter for 15 minutes on a boiling water-bath with water and a known volume (in excess) of N/10-HCl, the excess of the latter being then measured after cooling by means of N/10-KOH. The alkalinity found is expressed in c.c. of N-alkali per 100 grams of honey.

6. Determination of the Sugars.—These consist of saccharose and reducing sugars in varying proportions and are determined as follows :

(*a*) SACCHAROSE. 50 c.c. of the solution prepared as in (2) are clarified in a 100 c.c. flask with either basic lead acetate and sodium sulphate or alumina cream and then made up to the mark with water and filtered. The filtrate is polarised in a 20 cm. tube at the same time as the liquid prepared as follows :

Another quantity of 50 c.c. of the same solution is inverted with 5 c.c. of hydrochloric acid (sp. gr. 1·10) as usual, and then clarified, made up to 100 c.c., filtered and polarised at a known temperature.

By means of Clerget's formula (*see* General methods, p. 117) it is possible, from the data obtained, to calculate the quantity of saccharose in the honey.

(*b*) REDUCING SUGARS. In the liquid previously prepared for the polarisation before inversion the reducing sugars are determined by means of Fehling's solution (*see* General methods, p. 112) and calculated as invert sugar.

7. Dextrin.—The polarisations of solutions of honey before and after inversion furnish an indication of the presence or absence of dextrin, and, indirectly of that of commercial glucose, in honey. If the honey has a marked lævo-rotation, the presence of dextrin may be excluded, but if the rotation is either feebly negative or positive, a test should be made for dextrin, although some natural honeys free from dextrin do show similar behaviour.

5 grams of the honey are dissolved in 10 c.c. of water and the solution treated with 0·5 c.c. of 5% tannin solution and, when clarified, filtered. To part of the filtrate are added 2 drops of concentrated hydrochloric acid for each c.c. and then 10 times its volume of absolute alcohol. The appearance of milkiness (a faint turbidity may be neglected) indicates the presence of dextrin and hence of commercial glucose.

In doubtful cases, the test may be repeated by dissolving 40 grams of the honey in 50 c.c. of water in a 250 c.c. flask and adding absolute alcohol up to the mark. After a rest of two or three days, the precipitate is collected and tested by the reactions of dextrin and by the rotatory power.

8. Colour Reactions.—These are used for the detection of commercial invert sugar and are based on the colorations given by certain substances with methylfurfural and hydroxymethylfurfural, which occur in commercial invert sugar as decomposition products formed from the levulose during the inversion of saccharose by acids. Invert sugar prepared with invertase or by other special methods does not contain these decomposition products and consequently does not give the colour reactions. The most reliable of the latter are as follows :

(a) FIEHE'S REACTION.[1] About 5 grams of the honey are well mixed in a mortar with perfectly anhydrous, pure ether, the ethereal extract being evaporated in a porcelain dish at the ordinary temperature. The residue is moistened with a fresh solution of 1 gram of resorcinol in 100 grams of hydrochloric acid of density 1·19. If a marked cherry-red coloration, persistent for at least an hour, is obtained, commercial invert sugar is present ; slight transient colorations varying from red to orange are given by honey which has been more or less heated.

(b) JÄGERSCHMIDT'S REACTION.[2] 10 grams of the honey are well mixed in a porcelain mortar or dish with a certain quantity of pure acetone, 2 or 3 c.c. of the extract being then treated in a test-tube with an equal volume of concentrated hydrochloric acid and the mixture cooled under the tap. A deep violet-red coloration indicates presence of commercial invert sugar ; natural honey gives an amber coloration, gradually changing to reddish.

(c) ARMANI AND BARBONI'S REACTION.[3] From 2 to 4 grams of the honey are dissolved in a porcelain dish in 10 c.c. of distilled water and the solution treated in a test-tube immediately with 1 c.c. of benzidine acetate solution (1 gram of benzidine, 10 c.c. of concentrated acetic acid and 30 c.c. of water). If the honey is artificial or is composed of a mixture of invert sugar and natural honey, the liquid assumes a more or less intense golden coloration.

[1] *Zeitschr. Unt. Nahr- und Genuss-mittel*, 1908, XVI, p. 76.
[2] *Ibid.*, 1909, XVII, p. 113. [3] *Ann. Labor. chim. Centrale Gabelle*, Vol. VI, p. 8.

9. Lund's Reaction.[1]—This is based on the determination of the albuminous substances precipitable by tannic acid.   10 c.c. of the solution prepared as in (2) are treated in a graduated 50 c.c. tube with 5 c.c. of 0·5% tannic acid solution and made up with water to 40 c.c.   After careful shaking, the tube is closed with a cork and left for 24 hours, when the volume of the precipitate collected at the bottom of the tube is read.   With pure honey the volume is 1–4 c.c., whilst with artificial honey either no precipitate or only a trace is formed.

10. Diastatic Enzymes.[2]—100 grams of the honey are dissolved in 200 c.c. of distilled water previously boiled and cooled to 45°.

Into a test-tube, washed out with boiled water, are poured 10 c.c. of the unfiltered honey solution and exactly 1 c.c. of a fresh, clear 1% solution of soluble starch.[3]   After thorough mixing, the tube is immersed in a water-bath at 45° for exactly an hour.   A few drops of iodine solution (1 gram of iodine and 2 grams of potassium iodide in 200 c.c. of water) are then added and the colour at once assumed by the liquid observed.

If the colour is a little darker than that of the original honey solution, that is, from yellow to greenish or brownish yellow, the whole of the starch is saccharified by the diastatic enzymes of the honey ; if, however, the liquid is more or less dark blue, saccharification has not taken place and diastatic enzymes are absent or have been destroyed.   Finally, if the colour is red or brownish red or brown, a weakening of the diastatic power is indicated, this transforming the starch only into dextrin ; this is what happens with more or less heated centrifuged honey or with mixtures of natural with artificial honey.   If the results are uncertain, the test should be repeated.

11. Colouring Matters.—When treated with an acid, a solution of the honey in water (1 : 3) remains unchanged in colour in absence of added colouring matters, but if the latter are present the liquid becomes more or less dark red.

Colouring matters are also detected by treating the solution with a few drops of 10% potassium bisulphate solution and boiling the liquid for 10 minutes with a few threads of de-fatted wool immersed in it.   If, after washing with water, the wool is coloured yellow, a coal-tar colour is indicated ; it may be identified by its behaviour towards reagents, as indicated for wines (q.v.).

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The physical and chemical characters of *genuine honey* and the considerations on which conclusions as to adulterations are based, are as follows:

External characters.   Semi-liquid, viscous syrup, white to yellow to brown, taste sweet and aroma characteristic.

Microscopic test.   Pollen grains, starch granules and organs of the bee may be present.

Water.   The proportion varies within the wide limits, 8·90–21·50%, but as a rule does not exceed 20%.   The presence of more than 20% indicates

[1] *Zeitschr. Unt. Nahr- und Genuss-mittel*, 1909, XVII, p. 128.
[2] *Ibid.*, 1910, XIX, p. 65.
[3] Starch paste prepared as on p. 144 may also be used.

that water has been added or that the honey is one of the so-called immature honeys.

Dry matter other than sugar. This is less than 1·50% only in very rare cases and such a low value renders probable the presence of commercial invert sugar, glucose or saccharose, added as adulterant.

Acidity. This should not exceed 5 c.c. of N-alkali per 100 grams ; otherwise more or less advanced fermentation is indicated.

Ash. This varies between 0·10 and 0·35%, but there are honeys, especially Italian, with less ash than 0·10%, and others (from conifers) with as much as 0·80%. With these exceptions, however, proportions outside the above limits justify suspicion of adulteration with invert sugar, glucose, molasses, etc.

Sugars. Ordinary honey contains up to 8% of saccharose, but some varieties (from conifers) may contain 11%. Proportions larger than 8% in the one case, or than 11% in the other, usually denote addition of sugar ; it should, however, be borne in mind that bees fed with sugar or saccharine preparations may give honey with larger proportions of saccharose than those indicated.

Solutions of honey are usually lævo-rotatory, but with the varieties mentioned above may be dextro-rotatory. The proportion of reducing sugars, calculated as invert sugar, varies from 70 to 80%, but if marked quantities of saccharose are present, this proportion may fall to 60–70%.

Dextrin. A strong dextro-rotation after inversion and a positive reaction for dextrin indicate that the honey is adulterated with commercial liquid glucose, always assuming that the honey is not of a special type (conifer honey).

Colour reactions. A good criterion for judging of the genuineness of honey in so far as the addition of commercial invert sugar is concerned is furnished by the colour reactions, when these give *distinctly* positive results. In this case, since natural honey does not give the colour reactions, it may be concluded that the honey consists partially or wholly of commercial invert sugar.

Diastatic enzymes. When the colour reactions are positive, attention should be paid to the investigation of the diastatic enzymes, which should be carried out with great care. If this investigation gives negative results, the liquid in the tubes being coloured blue with iodine, the product consists of commercial invert sugar. It must, however, be remembered that natural honey which has been strongly heated is devoid of these enzymes and may also give the colour reactions, although *not intensely*. Heated honey, however, is coloured more or less deep brown and smells of caramel.

If the test for the enzymes gives positive results—the liquid in the tubes being coloured yellowish brown, red or reddish brown—and the colour reactions are given, the product most probably consists of a mixture of natural honey with commercial invert sugar.

Lund's reaction. This gives a positive result with natural honey, but little or no precipitate is obtained with artificial honeys.

In *conclusion,* the genuineness of a honey is proved by the whole of the above tests but never by any single test, however trustworthy

Chapter V

BEER [1]

Beer is a beverage of low alcoholic strength produced from malted barley (or malt), an infusion of which—termed *wort*—is treated with hops to give it a bitter flavour and fermented by means of yeast. Part of the malt is, however, often replaced by other cereals (wheat, rice, maize, etc.) or by various sugars (mostly glucose and invert sugar). As a rule a slight secondary fermentation takes place in beer, but this is not the case with beers which have been subjected to pasteurisation in order to improve their keeping qualities.

Besides water, the essential components of beer are alcohol and carbon dioxide, together with a considerable proportion of dissolved substances known collectively as extract and consisting principally of sugars (maltose), dextrins, proteins, glycerine, succinic acid, various inorganic and organic salts, and matters derived from the hops.

Examination of beer includes, in addition to observation of its external characters (smell, taste, colour, clearness, formation and retention of froth or " head "), determinations of the essential components and of any substances formed by alteration of the beer itself or added as adulterants.

Sampling.—The amount of beer usually required for analysis is about a litre. The sample is withdrawn from the cask either by means of a clean, dry siphon or by boring a small hole in the head of the cask, and is placed in clean, dry and, if possible, sterilised bottles, which should be immediately closed with good, new corks ; it is well to steep the latter for a few minutes in boiling water and then to dry them before use. The analysis should be carried out as soon as possible after sampling, the samples being kept meanwhile in a cool, dark place.

With almost all the determinations (naturally not that of the carbon dioxide), the beer should first be freed from the carbon dioxide present. This is done by pouring the beer repeatedly from one beaker to another or by shaking it vigorously in a large flask, the beer being afterwards filtered through a dry pleated filter.

1. Specific Gravity

The specific gravity of a beer, also termed " present gravity " or " attenuation gravity," is determined on the gas-free beer at 15·5° C. (60° F.)—with reference to water at the same temperature—by means of a specific gravity bottle or a Westphal balance (*see* Spirits).

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[1] This chapter has been very largely rewritten for the English edition.

2. Original Gravity, and Alcoholic Strength

The original gravity of a beer is the specific gravity of the wort prior to fermentation and is determined as follows : 100 c.c. of the gas-free beer, measured exactly in a 100 c.c. flask, are transferred quantitatively to a roomy flask—into which also the washings of the measuring flask are introduced—connected with a condenser. This flask is then heated, best by means of a rose burner, the distillate being collected in the 100 c.c. flask originally used for measuring the beer. The beer is kept boiling until about two-thirds of the liquid has distilled over, the distillate being then made up to volume at 15.5° C. with distilled water and mixed.

The specific gravity of the alcoholic liquid is then determined at 15.5° C. by means of a specific gravity bottle or Westphal balance and expressed with reference to water as 1000. Subtraction of this specific gravity from 1000 gives the degrees of " spirit indication," and the following table then shows the amount in degrees of the original wort (water = 1000) which has undergone fermentation.

The 100 c.c. flask is next washed out and the residue in the distillation flask transferred quantitatively to it and made up with water to 100 c.c. at 15.5° C. ; the specific gravity of this unfermented residue is added to the specific gravity of the portion which has undergone fermentation, the result being the original gravity of the beer.

TABLE XIX

Specific Gravity of Wort corresponding with Spirit Indication

Spirit Indication.	0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	0·00	0·42	0·85	1·27	1·70	2·12	2·55	2·97	3·40	3·82
1	4·25	4·67	5·10	5·52	5·95	6·37	6·80	7·22	7·65	8·07
2	8·50	8·94	9·38	9·82	10·26	10·70	11·14	11·58	12·02	12·46
3	12·90	13·34	13·78	14·22	14·66	15·10	15·54	15·98	16·42	16·86
4	17·30	17·75	18·21	18·66	19·12	19·57	20·03	20·48	20·94	21·39
5	21·85	22·30	22·76	23·21	23·67	24·12	24·58	25·03	25·49	25·94
6	26·40	26·86	27·32	27·78	28·24	28·70	29·16	29·62	30·08	30·54
7	31·00	31·46	31·93	32·39	32·86	33·32	33·79	34·25	34·72	35·18
8	35·65	36·11	36·58	37·04	37·51	37·97	38·44	38·90	39·37	39·83
9	40·30	40·77	41·24	41·71	42·18	42·65	43·12	43·59	44·06	44·53
10	45·00	45·48	45·97	46·45	46·94	47·42	47·91	48·39	48·88	49·36
11	49·85	50·35	50·85	51·35	51·85	52·35	52·85	53·35	53·85	54·35
12	54·85	55·36	55·87	56·38	56·89	57·40	57·91	58·42	58·93	59·44
13	59·95	60·46	60·97	61·48	61·99	62·51	63·01	63·52	64·03	64·54
14	65·10	65·62	66·14	66·66	67·18	67·70	68·22	68·74	69·26	69·78
15	70·30	70·83	71·36	71·89	72·42	72·95	73·48	74·01	74·54	75·07
16	75·60									

EXAMPLE : The specific gravity of the alcoholic distillate of a beer was found to be 982·16 and that of the unfermented residue 1014·28.

Spirit indication = 1000 − 982·16   =   7·84
Corresponding degrees of gravity lost =   34·90
Original gravity = 34·90 + 14·28   = 1049·2 or 49·2°.

In this country the specific gravity of a wort is often expressed in terms of " pounds per barrel." Since a barrel of water weighs 360 lbs. and the number of pounds per barrel represents the difference between the weights of a barrel of the wort and a barrel of water, it follows that:

Number of degrees of gravity = (number of lbs. per barrel) ÷ 0·36, and Number of lbs. per barrel = (number of degrees of gravity) × 0·36.

Thus, the original gravity of the beer considered above = 49·2 × 0·36 = 17·7 lbs. per barrel.

A check on the original gravity determination is furnished by the present gravity, which should not differ by much more than 0·2° from the value calculated from the specific gravities of the alcoholic distillate and the unfermented residue. In the above example, the present gravity of the beer should be very nearly equal to 14·28 − 7·84 = 6·44°, i.e., 1006·44.

When a beer contains more than 0·1% acid, determined by titration with N/10-ammonia solution with litmus paper as indicator and calculated as acetic acid, a correction is usually applied to the spirit indication. The amounts to be added to the spirit indication are shown in the following table for excess acidities varying from 0 to 1·09%. For instance, if the acidity is 0·28% (as acetic acid) the spirit indication found is to be increased by 0·24.

TABLE XX

Correction of Spirit Indication for Excess Acidity

Excess of Acetic Acid over 0·1%.	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
0·0	—	0·02	0·04	0·06	0·07	0·08	0·09	0·11	0·12	0·13
0·1	0·14	0·15	0·17	0·18	0·19	0·21	0·22	0·23	0·24	0·26
0·2	0·27	0·28	0·29	0·31	0·32	0·33	0·34	0·35	0·37	0·38
0·3	0·39	0·40	0·42	0·43	0·44	0·46	0·47	0·48	0·49	0·51
0·4	0·52	0·53	0·55	0·56	0·57	0·59	0·60	0·61	0·62	0·64
0·5	0·65	0·66	0·67	0·69	0·70	0·71	0·72	0·73	0·75	0·76
0·6	0·77	0·78	0·80	0·81	0·82	0·84	0·85	0·86	0·87	0·89
0·7	0·90	0·91	0·93	0·94	0·95	0·97	0·98	0·99	1·00	1·02
0·8	1·03	1·04	1·05	1·07	1·08	1·c9	1·10	1·11	1·13	1·14
0·9	1·15	1·16	1·18	1·19	1·21	1·22	1·23	1·25	1·26	1·28
1·0	1·29	1·31	1·33	1·35	1·36	1·37	1·38	1·40	1·41	1·42

The ratio of unfermented to fermented extract—in the above example, 14·28 : 34·90 = 1 : 2·44—is sometimes used by the brewer as an expression of the degree of fermentation.

3. Determination of the Ash

In a platinum dish on a water-bath, 25 or 50 c.c. of the beer are evaporated to dryness, the dry residue being carefully charred over a small flame, then incinerated slowly at a dull red heat and, when cold, weighed. The proportion of ash is expressed either in grams per 100 c.c. of the beer or as a percentage on the dry solids.

4. Determination of Chlorides (Sodium Chloride)

(1) 50 c.c. of the beer are evaporated to dryness in a platinum dish with about 0·5 gram of pure sodium carbonate. The residue is ignited over a small bunsen flame until no more organic fumes are evolved and only a black mass of cinder remains. The cinder is ground to powder and again heated carefully to dull redness. It is then warmed gently with 2 c.c. of concentrated nitric acid and about 20 c.c. of water and filtered. The chloride in the filtrate is precipitated and estimated in the usual way as silver chloride, the result being expressed as grains of sodium chloride per gallon of beer : $AgCl \times 0·408 = NaCl$.

(2) The chlorides may also be determined volumetrically by the following method,[1] which effects the removal of the phosphates from the beer : 50 c.c. of the beer are evaporated with 0·5 gram of barium carbonate and subsequently ignited to a black ash. The latter is extracted with hot water and filtered, the filtrate being then titrated with standard silver nitrate solution in presence of potassium chromate as indicator.

It should be pointed out that the above methods give the total chlorides calculated as sodium chloride and not the actual proportion of sodium chloride present. The latter is considerably lower than the former, since the amount of sodium in beer is always far·less than sufficient to correspond with the chlorine.

The amount of chlorides (calculated as sodium chloride) usually regarded as permissible in this country is 50 grains per gallon of the beer. These chlorides are derived partly from the water used and partly from the brewing materials ; an excessive proportion is sometimes introduced with glucose in the manufacture of which hydrochloric acid has been employed.

5. Acidity

The acidity of beer is due partly to various organic acids (especially lactic), partly to acid phosphates and, particularly in badly kept beers, partly to volatile acids (acetic). In some cases, the volatile acidity is determined separately from the fixed acidity.

1. **Total Acidity.**—50 or 100 c.c. of the beer, freed from the bulk of the carbon dioxide, are heated for half an hour at 40° to expel the residual gas and are then titrated with N/10-sodium hydroxide, neutral litmus paper or phenolphthalein being used as indicator ; when phenolphthalein is employed, it is well to add a slight excess of the alkali and then to run in N/10-sulphuric acid until the red coloration disappears. When, however, the liquid is too highly coloured to allow accurate observation of the point of neutrality, the procedure is as follows : to 20 c.c. of distilled water, previously boiled, are added 10–12 drops of alcoholic phenolphthalein solution and 0·2 c.c. of N/10-sodium hydroxide. The beer is then titrated with the decinormal alkali and, after each addition of the latter, six drops of the liquid are added to one drop of the indicator prepared as above, placed in the depression of a porcelain plate ; the titration is finished when this indicator is no longer decolorised in this way. The acidity is usually

[1] Race : *Journ. Soc. Chem. Industry*, 1908, XXVII, p. 544.

expressed as lactic acid per 100 c.c. of the beer (1 c.c. N/10-alkali = 0·009 gram of lactic acid) or as the number of c.c. of normal alkali required to neutralise 100 c.c. of beer.

2. Volatile Acidity.—50 or 100 c.c. of the beer, freed from carbon dioxide and treated with a little tannin, are distilled in a current of steam until acid no longer passes over (usually 100–200 c.c. of distillate are collected), the distillate being then titrated with decinormal alkali hydroxide in presence of phenolphthalein. The result is expressed as grams of acetic acid per 100 c.c. of the beer (1 c.c. N/10-alkali = 0 006 gram of acetic acid).

3. Fixed Acidity.—This is calculated by difference from the total and volatile acidities and is expressed as grams of lactic acid per 100 c.c. of the beer.

6. Determination of the Carbon Dioxide

It is not-usually necessary to determine the carbon dioxide in beer, since the external characters of the latter generally indicate if the gas is present in sufficient quantity. When, however, the determination is necessary, loss of gas during the extraction of the beer must be avoided. To this end, the vessels may be well cooled before they are opened, or special automatic extraction apparatus may be employed by means of which the beer is transferred directly, without loss of carbon dioxide, from the cask or bottle to the flask used in the determination.

A tared flask of approximately a litre capacity is charged with about 300 c.c. of the beer and then reweighed and closed with a two-holed stopper. Through the latter pass (1) a tube reaching to the liquid and communicating with the air by way of a soda-lime tube ; (2) a vertical condenser connected at the top successively with a calcium chloride tube, a bulb-tube containing sulphuric acid, a tared potash apparatus, and a calcium chloride tube. The beer is heated at first gently and then to boiling until all the carbon dioxide is expelled, the terminal calcium chloride tube being afterwards connected with an aspirator and a stream of air passed through the beer for some minutes. The increase in weight of the potash apparatus represents the carbon dioxide in the beer used.

7. Determination of the Glycerine

For this purpose 50 c.c. of the beer, deprived of gas, are treated as described for sweet wine (*q.v.*). The glycerine is calculated per 100 c.c.. of beer and sometimes per 100 parts by weight of alcohol.

8. Determination of the Maltose

In addition to maltose, beer contains small proportions of other reducing substances, which are however usually calculated as maltose. The gas-free beer is suitably diluted (dilution of 25 c.c. to 100 c.c. generally suffices) and the reducing substances determined by means of Fehling's solution, either gravimetrically or volumetrically :

(*a*) For the gravimetric method, 25 c.c. of the diluted beer are used and the procedure indicated in the chapter on sugars followed (*see* pp. 109

and 110).   For the calculation use is made of Table XIV (p. 111), the amount of maltose being referred to 100 c.c. of beer.

(b) For the volumetric method, the procedure described on p. 112 is employed.

9. Determination of the Dextrin

A mixture of 50 c.c. of the beer with 15 c.c. of hydrochloric acid (D 1·125) is diluted to 200 c.c. and heated for 2 hours on a boiling water-bath in a flask fitted with a long tube to serve as a condenser.   When cold, the liquid is neutralised exactly with caustic soda and made up to 250 c.c. or, with a beer rich in extract, to 300 c.c.   In 25 c.c. of this solution the glucose formed by inversion is determined by the method given on pp. 108 and 110 and calculated by means of Table XII (p. 110).   Since, however, part of the glucose found is derived from the inversion of the maltose, the amount of glucose found per 100 c.c. of the beer must be diminished by the amount of maltose present, multiplied by 1·053.   The remainder, multiplied by 0·9, represents the quantity of dextrin in 100 c.c. of the beer.

10. Determination of the Nitrogenous Substances

This is carried out on 25 or 50 c.c. of the beer, which is evaporated almost to dryness and the residue treated by the Kjeldahl process (see Vol. I, p. 122).   In the case of a beer rich in extract, it is advisable first to ferment it with a very small quantity of yeast, in order to avoid frothing on addition of sulphuric acid.   Albuminoids = nitrogen × 6·25.

The nitrogen is sometimes calculated per 100 parts of extract in the beer or per 100 parts of extract in the original wort.

11. Detection and Determination of Antiseptics

The methods of detecting and determining the preservatives commonly used in beer are as follows:

1. Sulphurous Acid.—200 c.c. of the beer, acidified with 5 c.c. of syrupy phosphoric acid, are distilled in a current of carbon dioxide, about 100 c.c. of distillate being collected in 50 c.c. of iodine solution (5 grams of iodine and 7·5 grams of potassium iodide per litre).   The iodine solution is afterwards acidified with hydrochloric acid and boiled to expel the excess of iodine, the sulphuric acid formed being then precipitated by means of barium chloride.   The presence of more than traces of sulphates indicates the addition of sulphite or sulphurous acid to the beer; in such case, the barium sulphate is collected and weighed as usual: $BaSO_4 \times 1·372 =$ weight of SO_2 per litre of the beer.

The determination may also be carried out volumetrically, the distillate being collected in a known volume of N/20-iodine solution, in which the excess of iodine is subsequently determined by titration with thiosulphate (see Wine, section 20, 1).

2. Boric Acid.—100 c.c. of the beer, rendered distinctly alkaline with sodium carbonate, are evaporated to dryness and the residue incinerated. The ash is dissolved in a little hydrochloric acid and the solution tested

with a strip of turmeric or, better, curcumin paper,[1] which is then dried at 100° on a clock-glass: in presence of boric acid, the paper turns red and when moistened with sodium carbonate solution it changes to blue.

The boric acid may be estimated by the colorimetric method described for wine (*q.v.*, section 23).

3. Oxalic Acid.—10 or 20 c.c. of the beer are acidified with acetic acid and treated with calcium chloride solution: a white precipitate indicates the presence of oxalic acid.

4. Salicylic Acid.—100 c.c. of the beer, acidified with 5 c.c. of dilute sulphuric acid, are shaken in a separating funnel twice with 50 c.c. of a mixture of ether and petroleum ether in equal volumes, a few drops of alcohol being added to facilitate the clarification of the solvent. The ethereal liquids are filtered into a flask and the solvent distilled off on a water-bath, the small amount of hot residue being treated with 4 or 5 c.c. of water and, with shaking, a few drops of dilute ferric chloride solution. The liquid is filtered through a moist filter and if the filtrate is violet, the presence of salicylic acid is indicated.

This coloration may, however, be due to maltol derived from torrefied malt. If, then, the reaction with ferric chloride is obtained, a portion of the aqueous solution of the residue from the ethereal extract should be tested with Millon's reagent [2]: a red coloration indicates salicylic acid, whilst no coloration shows that the reaction with ferric chloride is due to maltol.

5. Benzoic Acid.—250–500 c.c. of the beer, rendered alkaline with baryta water and mixed with about 50 grams of sand, are evaporated to dryness, the residue being treated in a mortar repeatedly with alcohol and a little dilute sulphuric acid. The alcoholic liquid, decanted off or filtered, is again rendered alkaline with baryta and the alcohol distilled off, the syrupy residue being acidified with sulphuric acid and extracted with ether. The ether is evaporated and the residue tested for benzoic acid by the following reactions:

(*a*) Part of the residue is dissolved in a little water and the solution heated on a water-bath with a drop of 2·5% ferric chloride solution and a drop of 0·3% hydrogen peroxide solution: in presence of benzoic acid, a violet coloration appears owing to the formation of salicylic acid.

(*b*) Another portion of the residue is dissolved on a clock-glass in a few drops of caustic soda solution, the liquid being then acidified, treated with a scrap of sodium amalgam and covered with another clock-glass, which is removed when evolution of hydrogen ceases: if benzoic acid were present, the characteristic odour of benzaldehyde will be observed.

6. Formaldehyde.—100 c.c. of the beer are distilled, the first 20–25 c.c. of distillate being tested for formaldehyde by the following reactions:

(*a*) About 15 c.c. of the distillate are treated with 1 c.c. of aqueous

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[1] For the preparation of this, *see* note on p. 8, this volume.

[2] Millon's reagent is prepared by dissolving 1 part of mercury in 1 part of nitric acid (D 1·41) first in the cold and afterwards at a gentle heat; the solution obtained is diluted with twice its volume of water and allowed to settle, the clear liquid being decanted off.

4% phenylhydrazine hydrochloride solution and 3–4 drops of a fresh 0·5% sodium nitroprusside solution, the liquid being then rendered alkaline with concentrated caustic soda solution : the presence of formaldehyde is indicated by an intense blue coloration, which gradually becomes red, especially on heating.[1]

(*b*) About 10 c.c. of the distillate are treated with about 0·1 gram of peptone, a drop of 5% ferric chloride solution and 10 c.c. of concentrated sulphuric acid : in presence of formaldehyde a deep violet ring forms between the two layers.

7. Fluorides.—100 c.c. of the beer are rendered feebly alkaline with ammonium carbonate and precipitated at the boiling point with 2–3 c.c. of 10% calcium chloride solution (or calcium hydroxide or barium acetate). After being boiled for five minutes the liquid is filtered and the precipitate washed, dried and gently ignited, together with the filter-paper, in a platinum crucible. When the latter is cold, 1 c.c. of concentrated sulphuric acid is added and the crucible immediately covered with a clock-glass, the lower side of which has been coated with paraffin wax and part of the wax scraped away with a pointed piece of hard wood. The crucible is then heated for about an hour on asbestos card or fireclay, the clock-glass being cooled meanwhile with pieces of ice so that the wax does not melt and the water formed by the ice absorbed from time to time with filter-paper. The glass is finally withdrawn and the wax removed to ascertain if any etching has taken place. Very slight etching may be rendered manifest by breathing on the clean, dry glass.

12. Detection of Artificial Sweetening Agents

This is carried out as in liqueurs (*q.v.*).

13. Detection of Extraneous Bitter Substances

Many bitter substances have been mentioned as substitutes for hops, but they are very seldom found in beer.

The complete examination for these bitter substances is long and complicated and does not always give certain results ; reference may be made to special publications on the subject.[2] A short test, which is sufficient in many cases, is as follows : 100 c.c. of the beer are evaporated to about one-half the volume, basic lead acetate being then added until no further precipitation occurs. The liquid is next filtered and the excess of lead in the filtrate precipitated with ammonium sulphate. If, after being again filtered, the liquid has a distinctly bitter flavour, the presence of extraneous bitter substances is indicated.

[1] Rimini : *Annali di Farmacoterapia e Chimica*, 1898, No. 3.
[2] *See* Dragendorff : *Zeitschr. anal. Chem.*, 1882, XXI. p. 137, and *Die gerichtl. chem. Ermittelung von Gifte*, 4th Edition, 1895 ; Kubicki : *Pharm. Zeitschr. für Russland*, 1873, p. 449, and *Zeitschr. anal. Chem.*, 1874, XIII. p. 67 ; König : *Chemie der menschl. Nahr- und Genussmittel*, 4th Edition, 1910, III. p. 302 ; Gerard et Bonn : *Traité prat. d'Analyse des Denrées alim.*, 1908, p. 78 ; Allen's *Commercial Organic Analysis*, 4th Edition, 1910, I. p. 161.

14. Detection of Injurious Metals

Beer may contain injurious metals, such as lead, copper, tin, zinc and iron (which imparts to the beer an unpleasant taste), derived from the vessels and plant used in its manufacture or from impurities of the raw materials ; in some cases arsenic has been found, this occurring as an impurity in the glucose used.

To detect all these metals with certainty, a quantity of the beer is evaporated to a syrup, the latter taken up in concentrated hydrochloric acid and the liquid heated and treated with successive small portions of potassium chlorate to oxidise the organic matter, and then boiled to eliminate the excess of chlorine and afterwards tested for the metals by the ordinary methods. For estimation of traces of arsenic, *see* p. 173.

15. Pasteurisation

To ascertain if a beer has been pasteurised, use is made of the following method, based on the fact that the enzymes present in the beer are either rendered inactive or considerably enfeebled as a result of pasteurisation : 20 c.c. of the beer are heated to boiling and, when cold again, treated with 20 c.c. of 20% saccharose solution ; at the same time another quantity of 20 c.c. of the beer (not heated) is treated with the same volume of the saccharose solution. The two liquids are left at the ordinary temperature for 24 hours, each being then treated with 0.5 c.c. of basic lead acetate, made up to 50 c.c. with water, filtered and polarised. If the two readings are markedly different, the original beer was not pasteurised ; on the other hand, virtual equality of the two polarisations indicates pasteurisation.

16. Forcing Test [1]

An indication of the stability of a beer may be obtained by " forcing " the latter, i.e., storing it at a temperature of about 80° F. (26.7° C.). The changes which occur gradually in the beer under ordinary conditions take place far more rapidly at the above temperature, so that examination of the beer after forcing renders it possible for the expert to predict the behaviour of the beer. The forcing may be carried out either in an ordinary beer bottle, or in a so-called forcing flask, which is fitted with a rubber stopper and with a side-tube bent to dip below the surface of a little mercury in a small vessel, or in any similar apparatus ; the receptacle should be thoroughly cleaned before being charged with the beer, which should completely fill it to the exclusion of air.

The forcing vessels may be placed either in an incubator or on the top of an oblong copper vessel (" forcing-tray ") filled with water and heated by a burner connected with a temperature-regulator.

After forcing for a period the length of which depends on the conditions the beer has to withstand and the time elapsing before its consumption, the beer is poured off so that the sediment is disturbed as little as possible. The beer is tasted to ascertain if it has remained sound or if acidity has developed, while its specific gravity is determined and compared with the

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[1] *See* Matthews and Lott : *The Microscope in the Brewery and Malt-house.*

value prior to forcing. Finally the yeasty sediment is examined under the microscope, attention being directed to any abnormalities in the form of the yeast cells and also to any bacteria which may be present.

Stock ales should be forced for four, or at least three, weeks, but for running ales a week is sufficient.

17. Estimation of Arsenic in Beer

Beer sometimes contains very small proportions of arsenic derived from the malt, sugars, hops, etc., used in brewing, and as the maximum amount allowable is one-hundredth of a grain of arsenic (As_2O_3) per gallon of the beer, it is advisable to keep a systematic check on the materials employed and also on the finished beer.

The presence of the organic matter hinders the liberation of the arsenic as hydrogen arsenide when the beer is placed either in a Marsh apparatus with zinc and dilute acid or in the cathode compartment of a cell in which dilute sulphuric acid is undergoing electrolytic decomposition. It is, therefore, necessary to destroy the organic matter before proceeding to the test. This may readily be done as follows: 50 c.c. of the beer, placed in a 500 c.c. long-necked hard-glass flask (Kjeldahl flask), are boiled over a small flame to a syrup, 25 c.c. of concentrated nitric acid (arsenic-free) being then added and the liquid gently heated until all violent action ceases; 3–5 c.c. (3 c.c. usually sufficient) of concentrated sulphuric acid (arsenic-free) are then added and the liquid again heated over a small flame until it darkens, 1–2 c.c. of the concentrated nitric acid being then added and the heating continued until the liquid darkens. This procedure is continued until the liquid remains quite colourless and fumes strongly of sulphuric acid. The solution is allowed to cool and then evaporated again with about 10 c.c. of distilled water to decompose any nitrosulphuric acid. The final liquid is diluted with a little water and cooled.

The solution prepared in this way may be tested by the Marsh-Berzelius method, but the simplest and most certain method consists in subjecting it to electrolysis by means of a platinum anode and a zinc cathode and passing the gas from the cathode compartment through a narrow tube heated at one part and cooled by water dropping on to filter-paper immediately beyond the flame. A convenient apparatus for this purpose, devised by William Thomson, is composed of a cylindrical unglazed porcelain cell, surrounded by an annular platinum anode and then by a closely-fitting glass beaker. Inside the porcelain cell fits a ground glass cover which is surmounted by a cylindrical funnel closed by a glass rod ground at the bottom and is also traversed by a rubber stopper carrying the connecting wire fused into the zinc cathode. The cover is also fitted with a gas-delivery tube connected through a small calcium chloride tube (containing also a small roll of lead acetate paper) with the tube in which the hydrogen arsenide is decomposed by heating.

The anode compartment is filled and the cathode compartment partially filled with pure dilute sulphuric acid (1 : 8) and a current of about 3·5 amperes passed for about 5 minutes to expel all the air from the apparatus, which is best kept cool by standing in a fairly large vessel of water. The

drawn-out tube (this may conveniently be of transparent silica) is then heated at one point and cooled immediately beyond ; after about 10 minutes the cooled part should show no trace of an arsenic mirror if the apparatus and sulphuric acid are free from arsenic. When this is the case, the liquid prepared from the beer is introduced quantitatively into the cell, care being taken that no air is admitted. The current is allowed to pass for a further period of 45 minutes, all the arsenic present being then deposited.

The mirror on the tube is compared with a series of standard mirrors prepared in a similar manner from 0·001, 0·002, 0·003, . . . 0·01 milligram of As_2O_3. To obtain these, 0·1 gram of As_2O_3 is dissolved in water in presence of a very small amount of pure caustic soda and the solution made up to 1 litre, 10 c.c. of this being afterwards diluted with water to 1 litre ; each 1 c.c. of this second solution contains 0·001 milligram of As_2O_3.

In the hands of an experienced operator this method gives accurate results.

CHAPTER VI

WINE

Wine is the name given to the alcoholic beverage obtained by the complete or partial alcoholic fermentation of the *must* or juice of the grape, fresh or slightly turned, without addition of any extraneous substances.

The essential and normal components of wine are the same in almost all varieties and types; the respective proportions alone vary in different kinds of wine, which may be grouped in three principal categories, namely, *ordinary wine, sweet wine* and *vins de coupage* (used for improving weak wines).

These components are alcohol, glycerine, sugars, colouring matters, albuminoid and tannin substances, inorganic salts (phosphates, sulphates and chlorides of potassium, sodium, magnesium, calcium and aluminium), non-volatile organic acids (especially tartaric, malic, succinic and lactic, partly free and partly combined as salts), volatile acids (especially acetic) and esters, the latter being the source of the particular perfume or bouquet of the wine.

Analysis of wine may be directed to the following ends:

(*a*) To establish its commercial value. In this case great importance attaches to the examination of the objective characters and to the determination of some of the more important constituents, e.g., the alcohol, extract, sugars (for sweet wines), acidity and intensity of colour (for *vins de coupage*).

(*b*) To ascertain if the wine is normal or has undergone alterations owing to defects in the prime materials employed (grapes turned bad, or unripe, or attacked by parasites, etc.), or to faults in the manufacture or storage. In this case, besides the objective and microscopic examinations, use is also made, where necessary, of determinations of the normal components of wine as in case (*c*).

(*c*) To determine if the wine has been adulterated so that it cannot be regarded as genuine. The adulteration may refer to the natural components of the wine and it is then necessary to ascertain if these are present in the absolute and relative amounts proper to the particular kind of wine, or it may be due to the addition either of excessive doses of permissible substances or of substances quite foreign to the normal composition of the wine. In such cases, in addition to the determinations indicated above, it will be necessary to make a more or less complete analysis, determinations being made of the glycerine, volatile acidity, ash, plastering, sulphurous acid, alkalinity of the ash, organic acids (mainly tartaric and citric), phosphating, salting and glucose, and tests for extraneous substances, such

175

as colouring, antiseptic and sweetening materials, free mineral acids, heavy metals, barium and strontium.

If one or more of the tests demonstrates that the wine is not genuine it will be superfluous, unless expressly required, to carry out the other determinations.

In certain special cases it may be necessary to supplement the estimations mentioned above by those of other constituents of the wine, such as tannic, malic, lactic and succinic acids. The results obtained exhibit, however, some uncertainty and the deductions drawn are thus not always concordant.

The determinations made on samples of wine should be carried out immediately, the results obtained being expressed in grams per litre of wine at 15° C., excepting in the case of (1) the alcohol, which is given in c.c. or grams per 100 c.c., and (2) the alkalinity, which is described as c.c. of N-alkali per litre. Four decimal figures are given with the specific gravity, three with the ash and two with other magnitudes.

Sampling and Preparation of the Sample. The amount of wine necessary varies according to the determinations required. For the principal tests a litre is wanted and for a complete analysis or for special investigations correspondingly more. The official directions for sampling wine for sale or consumption are as follows :

The quantity of wine for chemical analysis should be at least four bottles of about a litre each. Transparent bottles should be used and they should be rinsed first with water and then with the wine so that no trace of any substance previously present can remain. The bottles should be filled, carefully stoppered with new corks of good quality and provided with sealing-wax seals and with a label giving all the particulars necessary for the identification of the sample. Further, on a special sheet are given the name and address of the holder of the wine, the capacity of the casks or other vessels from which the sample is drawn and the extent to which they are filled, any production of scum (so-called " fleurs de vin ") being noted and, if possible, the type, place of origin and year of production of the wine itself.

The sample should be sent as rapidly as possible to the laboratory, and when the analysis is not to be carried out immediately the bottles are stored horizontally and in a cool, but not excessively cold, place. Turbid samples are either left for some time and then decanted or filtered prior to analysis, the residue being examined separately if necessary. The determination of sulphur dioxide should be made before filtration and as soon as the bottle is opened.

If it is desired to keep the residue of the sample analysed, it may be pasteurised by heating it in a closed vessel at 75° C. for an hour.

1. External Examination

The external characters, namely, the colour, brilliancy, smell and taste, are noted as soon as the bottle is opened, the most suitable temperature being 15° C. for white wines and 17° for red ones. If carbon dioxide is

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liberated when the vessel is opened, this is expelled by agitation before analysis.

Note is made of the colour—white or red—and of its intensity, which (with " vins de coupage ") may be measured (*see* 12).

The brilliancy, which is estimated by looking through a layer of the wine of suitable thickness, indicates if the wine is sound and has kept well. If the sample is turbid, it is left for some time and then decanted or filtered before analysis ; in many cases it may be advisable to examine the deposit microscopically.

As regards the odour, abnormality often furnishes useful indications of alterations or adulterations to which the wine has been subjected (e.g., the smell of vinegar, sulphur dioxide, etc.).

The wine is tasted to ascertain if it is sweet or dry, and if there is any abnormality of taste indicative of alteration or adulteration. Thus, the alcoholic taste may not harmonise with the quality of the wine, or there may be acidity caused by souring of the wine, harshness due to tannin, a flavour from the lees or cask or from carbon dioxide, abnormal sweetness, a taste of sulphur dioxide, etc.

2. Determination of the Specific Gravity

This is measured at 15° C., with respect to water at the same temperature, by means of a tested Westphal balance (*see* Spirituous Liquors) sensitive to the fourth decimal figure.

3. Determination of the Alcohol

The alcohol is determined either by distilling the wine and calculating from tables the alcoholic content of the distillate from its specific gravity at 15° C. or by means of a special apparatus known by the name of ebullioscope. This gives the *alcoholic degree of the wine* ; with sweet wines, a calculation is sometimes also made of the *potential alcoholic strength*, which is the sum of the alcohol found and of that derivable from the fermentation of the sugars still present.[1]

1. Distillation Method.—Exactly 100 c.c. of the wine are measured at 15° C. in a graduated flask and introduced into a conical or round-bottomed flask of about 300 c.c. capacity, the graduated flask being rinsed out several times with a little water. The flask is then connected with a condenser and heated over a gauze with a small flame until the distillate occupies more than two-thirds of the graduated flask. The distillate is then carefully shaken and made up with water to exactly 100 c.c. at 15° C., its specific gravity at this temperature being determined by the Westphal balance. Table XXI then gives the percentage of alcohol by volume

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[1] Thus, for Customs purposes [in Italy], the alcoholic strength (*potential*) of sweet wines which contain more than 1% of unfermented sugar and in which the total sugar (that present plus that corresponding with the alcohol in the wine) exceeds 26% is calculated by adding to the alcohol contained in the wine that corresponding with the sugars present (percentage of sugar multiplied by 0·63). For instance, with a wine containing 11·5% of alcohol by volume and 8·50% of sugars, the alcoholic strength (*potential*) will be 11·50 + 8·50 × 0·63 = 16·85%.

(*alcoholic degree by volume*) or the grams of alcohol per 100 c.c. of wine (*alcoholic degree by weight*).[1]

If the wine is highly alcoholic, it is convenient first of all to dilute it with water to double its volume.

With an acid wine, it is well to prevent distillation of the volatile acids by neutralising the acidity with magnesium oxide or a few drops of concentrated caustic soda solution. Frothing is prevented by leaving the wine slightly acid or by addition of tannin.

2. Malligand's Ebullioscope.—This is based on the principle that aqueous alcoholic mixtures boil at temperatures which are more or less low compared with that of water in accordance with their alcoholic content.

The apparatus (Fig. 50) consists of a small conical metallic boiler C, carrying at the bottom a thermo-siphon consisting of a hollow metal ring A heated by a spirit lamp L. The boiler is closed by a screw cover pierced by two orifices, one for a small condenser R and the other for a thermometer bent at right-angles T; a graduated scale moves along the horizontal arm of the thermometer.
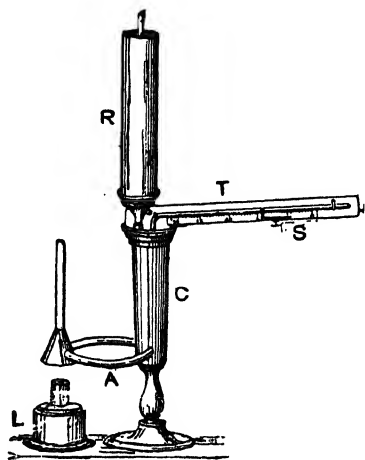
FIG. 50

The procedure is as follows : Water is introduced into the boiler up to a certain level marked inside, the depth of water being insufficient to immerse the thermometer bulb. The cover is then screwed on, the condenser filled with cold water and the lamp lighted. When the extremity of the mercury column fails to move any further, the scale, which is graduated from 0 to 25, is adjusted so that the zero corresponds with the meniscus of the mercury column and fixed in this position by means of a screw. The zero should be determined for each test, or for each series of tests at least, since it varies with the atmospheric pressure.

The water is then poured away and the boiler rinsed two or three times with the wine to be tested and filled up with the latter to a second mark in the upper part of the boiler, the amount of liquid in this case being sufficient to cover the thermometer bulb. The lid is screwed on, the condenser charged with cold water and the wine heated as before. The reading of the mercury on the scale gives directly the alcoholic strength (by volume) of the wine. Care must be taken that the intensity of the flame is the same during the determination of the alcohol as during the determination of the zero, the length of the wick and the amount of spirit in the lamp being kept constant.

[1] When the specific gravity is determined at a temperature other than 15°, the necessary corrections are obtained from tables given by G. Tommasi (*Ann. R. staz. chim. agr. sperim. di Roma*, 1913, VI, p. 157).

TABLE XXI

Alcohol Table

Sp. gr. at 15°/15°.	% of Alcohol by Weight.	% of Alcohol by Volume.	Grams of Alcohol per 100 c.c.	Sp. gr. at 15°/15°.	% of Alcohol by Weight.	% of Alcohol by Volume.	Grams of Alcohol per 100 c.c.
0·9999	0·05	0·07	0·05	0·9959	2·22	2·79	2·21
8	0·11	0·13	0·11	8	2·28	2·86	2·27
7	0·16	0·20	0·16	7	2·34	2·93	2·32
6	0·21	0·27	0·21	6	2·39	3·00	2·38
5	0·26	0·33	0·26	5	2·45	3·07	2·43
4	0·32	0·40	0·32	4	2·50	3·14	2·49
3	0·37	0·47	0·37	3	2·56	3·21	2·55
2	0·42	0·53	0·42	2	2·62	3·28	2·60
1	0·48	0·60	0·47	1	2·68	3·35	2·66
0	0·53	0·67	0·53	0	2·73	3·42	2·72
0·9989	0·58	0·73	0·58	0·9949	2·79	3·49	2·77
8	0·64	0·80	0·64	8	2·84	3·56	2·82
7	0·69	0·87	0·69	7	2·90	3·64	2·88
6	0·74	0·93	0·74	6	2·96	3·71	2·94
5	0·80	1·00	0·80	5	3·02	3·78	3·00
4	0·85	1·07	0·85	4	3·08	3·85	3·06
3	0·90	1·14	0·90	3	3·14	3·93	3·12
2	0·96	1·20	0·96	2	3·19	4·00	3·17
1	1·01	1·27	1·01	1	3·25	4·07	3·23
0	1·06	1·34	1·06	0	3·31	4·14	3·29
0·9979	1·12	1·41	1·12	0·9939	3·37	4·22	3·35
8	1·17	1·48	1·17	8	3·43	4·29	3·40
7	1·23	1·54	1·22	7	3·49	4·36	3·46
6	1·28	1·61	1·28	6	3·55	4·43	3·52
5	1·34	1·68	1·33	5	3·60	4·51	3·58
4	1·39	1·75	1·39	4	3·66	4·58	3·64
3	1·45	1·82	1·44	3	3·72	4·65	3·69
2	1·50	1·88	1·50	2	3·78	4·73	3·75
1	1·56	1·95	1·55	1	3·84	4·80	3·81
0	1·61	2·02	1·60	0	3·90	4·88	3·87
0·9969	1·67	2·09	1·66	0·9929	3·95	4·95	3·93
8	1·72	2·16	1·71	8	4·02	5·03	3·99
7	1·78	2·23	1·77	7	4·08	5·10	4·05
6	1·83	2·30	1·82	6	4·14	5·18	4·11
5	1·89	2·37	1·88	5	4·20	5·25	4·17
4	1·94	2·44	1·93	4	4·26	5·33	4·23
3	2·00	2·51	1·99	3	4·32	5·40	4·29
2	2·05	2·58	2·04	2	4·39	5·48	4·35
1	2·11	2·65	2·10	1	4·45	5·55	4·41
0	2·17	2·72	2·16	0	4·51	5·63	4·47

TABLE XXI—*continued*

Sp. gr. at 15°/15°.	% of Alcohol by Weight.	% of Alcohol by Volume.	Grams of Alcohol per 100 c.c.	Sp. gr. at 15°/15°.	% of Alcohol by Weight.	% of Alcohol by Volume.	Grams of Alcohol per 100 c.c.
0·9919	4·57	5·70	4·53	0·9879	7·15	8·89	7·06
8	4·63	5·78	4·59	8	7·22	8·98	7·12
7	4·69	5·86	4·65	7	7·29	9·06	7·19
6	4·75	5·93	4·71	6	7·36	9·15	7·26
5	4·81	6·01	4·77	5	7·42	9·23	7·33
4	4·88	6·09	4·83	4	7·49	9·32	7·39
3	4·94	6·16	4·89	3	7·56	9·40	7·46
2	5·00	6·24	4·95	2	7·63	9·48	7·53
1	5·06	6·32	5·01	1	7·70	9·57	7·60
0	5·13	6·40	5·08	0	7·77	9·66	7·66
0·9909	5·19	6·47	5·14	0·9869	7·84	9·74	7·73
8	5·25	6·55	5·20	8	7·91	9·83	7·80
7	5·32	6 63	5·26	7	7·98	9·91	7·87
6	5·38	6·71	5·32	6	8·05	10·00	7·94
5	5·44	6·79	5·38	5	8·12	10·09	8·00
4	5·51	6·86	5·45	4	8·19	10·17	8·07
3	5·57	6·94	5·51	3	8·26	10·26	8·14
2	5·63	7·02	5·57	2	8·33	10·35	8·21
1	5·70	7·10	5·64	1	8·41	10·43	8·28
0	5·76	7·18	5·70	0	8·48	10·52	8·35
0·9899	5·83	7·26	5·76	0·9859	8·55	10·61	8·42
8	5·89	7·34	5·83	8	8·62	10·70	8·49
7	5·96	7·42	5·89	7	8·69	10·79	8·56
6	6·02	7·50	5·95	6	8·76	10·88	8·63
5	6·09	7·58	6·02	5	8·84	10·96	8·70
4	6·15	7·66	6·08	4	8·91	11·05	8·77
3	6·22	7·74	6·14	3	8·98	11·14	8·84
2	6·28	7·82	6·21	2	9·06	11·23	8·91
1	6·35	7·90	6·27	1	9·13	11·32	8·98
0	6·41	7·99	6·34	0	9·20	11·41	9·06
0·9889	6·48	8·07	6·40	0·9849	9·28	11·50	9·13
8	6·55	8·15	6·47	8	9·35	11·59	9·20
7	6·61	8·23	6·53	7	9·42	11·68	9·27
6	6·68	8·31	6·59	6	9·50	11·77	9·34
5	6·75	8·40	6·66	5	9·57	11·86	9·42
4	6·81	8·48	6·73	4	9·65	11·95	9·49
3	6·88	8·56	6·79	3	9·72	12·05	9·56
2	6·95	8·64	6·86	2	9·80	12·14	9·63
1	7·02	8·73	6·93	1	9·87	12·23	9·70
0	7·08	8·81	6·99	0	9·94	12·32	9·78

TABLE XXI—*continued*

Sp. gr. at 15°/15°.	% of Alcohol by Weight.	% of Alcohol by Volume.	Grams of Alcohol per 100 c.c.	Sp. gr. at 15°/15°.	% of Alcohol by Weight.	% of Alcohol by Volume.	Grams of Alcohol per 100 c.c.
0·9839	10·02	12·41	9·85	0·9799	13·16	16·24	12·89
8	10·10	12·50	9·92	8	13·25	16·34	12·97
7	10·17	12·59	9·99	7	13·33	16·44	13·05
6	10·25	12·69	10·07	6	13·41	16·54	13·13
5	10·32	12·78	10·14	5	13·49	16·64	13·20
4	10·40	12·88	10·22	4	13·57	16·74	13·28
3	10·48	12·97	10·29	3	13·66	16·84	13·36
2	10·55	13·06	10·36	2	13·74	16·94	13·44
1	10·63	13·16	10·44	1	13·82	17·04	13·52
0	10·71	13·25	10·52	0	13·90	17·14	13·60
0·9829	10·78	13·34	10·59	0·9789	13·98	17·24	13·68
8	10·86	13·44	10·66	8	14·07	17·34	13·76
7	10·94	13·53	10·74	7	14·15	17·44	13·84
6	11·01	13·63	10·81	6	14·23	17·54	13·92
5	11·09	13·72	10·89	5	14·32	17·64	14·00
4	11·17	13·82	10·96	4	14·40	17·74	14·08
3	11·25	13·91	11·04	3	14·48	17·84	14·15
2	11·33	14·01	11·12	2	14·56	17·94	14·23
1	11·40	14·10	11·19	1	14·65	18·04	14·31
0	11·48	14·20	11·27	0	14·73	18·14	14·39
0·9819	11·56	14·29	11·34	0·9779	14·81	18·24	14·47
8	11·64	14·39	11·42	8	14·90	18·34	14·55
7	11·72	14·48	11·49	7	14·98	18·44	14·63
6	11·80	14·58	11·57	6	15·06	18·54	14·71
5	11·88	14·68	11·65	5	15·15	18·64	14·79
4	11·96	14·77	11·72	4	15·23	18·74	14·87
3	12·04	14·87	11·80	3	15·31	18·84	14·95
2	12·12	14·97	11·88	2	15·40	18·94	15·03
1	12·20	15·07	11·96	1	15·48	19·04	15·11
0	12·28	15·16	12·03	0	15·56	19·14	15·19
0·9809	12·36	15·26	12·11	0·9769	15·65	19·24	15·27
8	12·44	15·36	12·19	8	15·73	19·34	15·35
7	12·52	15·46	12·27	7	15·81	19·44	15·43
6	12·60	15·55	12·34	6	15·90	19·55	15·51
5	12·68	15·65	12·42	5	15·98	19·65	15·59
4	12·76	15·75	12·50	4	16·06	19·75	15·67
3	12·84	15·85	12·58	3	16·15	19·85	15·75
2	12·92	15·95	12·65	2	16·23	19·95	15·83
1	13·00	16·04	12·73	1	16·32	20·05	15·91
0	13·08	16·14	12·81	0	16·40	20·15	15·99

WINE

Table XXI—*continued*

Sp. gr. at 15°/15°.	% of Alcohol by Weight.	% of Alcohol by Volume.	Grams of Alcohol per 100 c.c.	Sp. gr. at 15°/15°.	% of Alcohol by Weight.	% of Alcohol by Volume.	Grams of Alcohol per 100 c.c.
0·9759	16·48	20·25	16·07	0·9729	18·98	23·24	18·45
8	16·57	20·35	16·15	8	19·06	23·34	18·52
7	16·65	20·45	16·23	7	19·14	23·44	18·60
6	16·73	20·55	16·31	6	19·22	23·54	18·68
5	16·82	20·65	16·39	5	19·30	23·63	18·76
4	16·90	20·75	16·47	4	19·39	23·73	18·84
3	16·98	20·86	16·55	3	19·47	23·83	18·91
2	17·07	20·96	16·63	2	19·55	23·93	18·99
1	17·15	21·06	16·71	1	19·63	24·02	19·07
0	17·23	21·16	16·79	0	19·71	24·12	19·14
0·9749	17·32	21·26	16·87	0·9719	19·79	24·22	19·22
8	17·40	21·36	16·95	8	19·87	24·32	19·30
7	17·49	21·46	17·03	7	19·95	24·41	19·37
6	17·57	21·56	17·11	6	20·04	24·51	19·45
5	17·65	21·66	17·19	5	20·12	24·60	19·53
4	17·73	21·76	17·27	4	20·20	24·70	19·60
3	17·82	21·86	17·35	3	20·28	24·80	19·68
2	17·90	21·96	17·42	2	20·36	24·89	19·76
1	17·98	22·06	17·50	1	20·44	24·99	19·83
0	18·07	22·16	17·58	0	20·52	25·08	19·91
0·9739	18·15	22·26	17·66	0·9709	20·60	25·18	19·98
8	18·23	22·35	17·74	8	20·68	25·27	20·06
7	18·32	22·45	17·82	7	20·76	25·37	20·13
6	18·40	22·55	17·90	6	20·84	25·47	20·21
5	18·48	22·65	17·98	5	20·92	25·56	20·28
4	18·56	22·75	18·05	4	21·00	25·66	20·36
3	18·65	22·85	18·13	3	21·08	25·75	20·43
2	18·73	22·95	18·21	2	21·16	25·84	20·51
1	18·81	23·05	18·29	1	21·24	25·94	20·58
0	18·89	23·14	18·37	0	21·32	26·03	20·66

With "vins de coupage" or slightly sweet wines, it is best to dilute to double the volume, and with sweet wines to four times the volume, the result obtained being suitably corrected.

Malligand's ebullioscope gives results sufficiently accurate for commercial purposes, provided ordinary sound wines are employed. In the case of sweet wines the results are rather above the true values, the error being diminished but not eliminated by dilution. When the alcoholic strength of a wine is determined by the ebullioscope, mention should be made of this fact on the report of the analysis.

4. Determination of the Extract

The extract of a wine is the fixed residue obtained after evaporation of the volatile matters (*total extract*). In ordinary wines the principal components of the extract are glycerine, tannin, potassium bitartrate,

colouring matters and small proportions of sugars. With sweet wines, which contain larger quantities of sugars, the extract is calculated by subtracting the sugars from the total extract (*non-saccharine extract*).

The extract may be determined either directly or indirectly :

1. Indirect Method.—The specific gravities of the wine and of the alcoholic distillate being indicated by p and p' respectively, that of the wine freed from alcohol and then made up to its original volume is calculated from the expression :

$$P = 1 + p - p'.$$

The value of the extract E per 100 c.c. corresponding with this value P is then determined from Table XXII. If E is equal to or greater than 4, it represents the grams of extract per 100 c.c. of the wine.[1] If, however, E is less than 4, the result of the indirect determination is regarded only as a preliminary value, the direct method being then employed.

The indirect method is used especially for sweet and liqueur wines.

2. Direct Method.—Two cases are distinguished :

(*a*) If the indirect extract E calculated as above does not exceed 3, the direct determination is made by evaporating 50 c.c. of the wine in a tared platinum dish on a boiling water-bath having an aperture 60 mm. in diameter. This dish should be flat-bottomed and have a diameter of 85 mm. and a height of 20 mm., with a weight of about 20 grams. When the residue becomes viscous (it being then necessary to watch the evaporation continuously), the dish is dried outside with filter-paper and left for $2\frac{1}{2}$ hours on a little tripod 1 cm. high in a small steam-oven. It is then cooled and the weight of the extract determined.

(*b*) If the extract E calculated indirectly lies between 3 and 4, such volume of the wine is measured out from a burette as will give not more than 1·5 gram of extract, distilled water being then added to bring the volume up to 50 c.c. The volume of wine to be taken is found by dividing 150 by the value of E found in the table. The diluted wine is evaporated in a tared dish as described above and the extract per litre of the wine calculated.

In order that comparable values may be obtained for the extracts of wines, the method given must be strictly followed. Besides undergoing alteration when heated, some of the substances composing the extract of wine, e.g., glycerine, exhibit appreciable vapour pressures, so that they are expelled to greater or less extents according to the duration and conditions of the evaporation. Hence, besides observing strictly the form and dimensions of the capsule, the heating surface and the quantity of wine to be used, it is well to use for the complete drying of the extract a water-bath with compartments 10 cm. wide, 10 cm. deep and 5 cm. high with a shutter having two series of apertures 2 mm. in diameter for the passage of air and steam.

[1] The table used for the calculation of the extract is based on the density of aqueous saccharose solutions, so that the extract thus calculated has only a conventional value. Other tables exist which are based on the densities of solutions of grape must, but in view of the varying proportions in which the components of the must occur in the extracts of wines of different types, such tables also have no more than a conventional value.

TABLE XXII

Total Extract from Sp. Gr. of Alcohol-free Residue

Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.
1.0000	0.00	1.0040	1.03	1.0080	2.07	1.0120	3.10	1.0160	4.13
1	0.03	1	1.06	1	2.09	1	3.12	1	4.16
2	0.05	2	1.08	2	2.12	2	3.15	2	4.19
3	0.08	3	1.11	3	2.14	3	3.18	3	4.21
4	0.10	4	1.13	4	2.17	4	3.20	4	4.24
5	0.13	5	1.16	5	2.19	5	3.23	5	4.26
6	0.15	6	1.18	6	2.22	6	3.26	6	4.29
7	0.18	7	1.21	7	2.25	7	3.28	7	4.31
8	0.20	8	1.24	8	2.27	8	3.31	8	4.34
9	0.23	9	1.26	9	2.30	9	3.33	9	4.37
1.0010	0.26	1.0050	1.29	1.0090	2.32	1.0130	3.36	1.0170	4.39
1	0.28	1	1.32	1	2.35	1	3.38	1	4.42
2	0.31	2	1.34	2	2.38	2	3.41	2	4.44
3	0.34	3	1.37	3	2.40	3	3.43	3	4.47
4	0.36	4	1.39	4	2.43	4	3.46	4	4.50
5	0.39	5	1.42	5	2.45	5	3.49	5	4.52
6	0.41	6	1.45	6	2.48	6	3.51	6	4.55
7	0.44	7	1.47	7	2.50	7	3.54	7	4.57
8	0.46	8	1.50	8	2.53	8	3.56	8	4.60
9	0.49	9	1.52	9	2.56	9	3.59	9	4.63
1.0020	0.52	1.0060	1.55	1.0100	2.58	1.0140	3.62	1.0180	4.65
1	0.54	1	1.57	1	2.61	1	3.64	1	4.68
2	0.57	2	1.60	2	2.63	2	3.67	2	4.70
3	0.59	3	1.63	3	2.66	3	3.69	3	4.73
4	0.62	4	1.65	4	2.69	4	3.72	4	4.75
5	0.64	5	1.68	5	2.71	5	3.75	5	4.78
6	0.67	6	1.70	6	2.74	6	3.77	6	4.81
7	0.69	7	1.73	7	2.76	7	3.80	7	4.83
8	0.72	8	1.76	8	2.79	8	3.82	8	4.86
9	0.75	9	1.78	9	2.82	9	3.85	9	4.88
1.0030	0.77	1.0070	1.81	1.0110	2.84	1.0150	3.87	1.0190	4.91
1	0.80	1	1.83	1	2.87	1	3.90	1	4.94
2	0.82	2	1.86	2	2.89	2	3.93	2	4.96
3	0.85	3	1.88	3	2.92	3	3.95	3	4.99
4	0.87	4	1.91	4	2.94	4	3.98	4	5.01
5	0.90	5	1.94	5	2.97	5	4.00	5	5.04
6	0.93	6	1.96	6	3.00	6	4.03	6	5.06
7	0.95	7	1.99	7	3.02	7	4.06	7	5.09
8	0.98	8	2.01	8	3.05	8	4.08	8	5.11
9	1.00	9	2.04	9	3.07	9	4.11	9	5.14

TABLE XXII—*continued*

Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.
1·0200	5·17	1·0240	6·20	1·0280	7·24	1·0320	8·27	1·0360	9·31
1	5·19	1	6·23	1	7·26	1	8·30	1	9·34
2	5·22	2	6·25	2	7·29	2	8·33	2	9·36
3	5·25	3	6·28	3	7·32	3	8·35	3	9·39
4	5·27	4	6·31	4	7·34	4	8·38	4	9·42
5	5·30	5	6·33	5	7·37	5	8·40	5	9·44
6	5·32	6	6·36	6	7·39	6	8·43	6	9·47
7	5·35	7	6·38	7	7·42	7	8·46	7	9·49
8	5·38	8	6·41	8	7·45	8	8·48	8	9·52
9	5·40	9	6·44	9	7·47	9	8·51	9	9·55
1·0210	5·43	1·0250	6·46	1·0290	7·50	1·0330	8·53	1·0370	9·57
1	5·45	1	6·49	1	7·52	1	8·56	1	9·60
2	5·48	2	6·51	2	7·55	2	8·59	2	9·62
3	5·51	3	6·54	3	7·58	3	8·61	3	9·65
4	5·53	4	6·56	4	7·60	4	8·64	4	9·68
5	5·56	5	6·59	5	7·63	5	8·66	5	9·70
6	5·58	6	6·62	6	7·65	6	8·69	6	9·73
7	5·61	7	6·64	7	7·68	7	8·72	7	9·75
8	5·64	8	6·67	8	7·70	8	8·74	8	9·78
9	5·66	9	6·70	9	7·73	9	8·77	9	9·80
1·0220	5·69	1·0260	6·72	1·0300	7·76	1·0340	8·79	1·0380	9·83
1	5·71	1	6·75	1	7·78	1	8·82	1	9·86
2	5·74	2	6·77	2	7·81	2	8·85	2	9·88
3	5·77	3	6·80	3	7·83	3	8·87	3	9·91
4	5·79	4	6·82	4	7·86	4	8·90	4	9·93
5	5·82	5	6·85	5	7·89	5	8·92	5	9·96
6	5·84	6	6·88	6	7·91	6	8·95	6	9·99
7	5·87	7	6·90	7	7·94	7	8·97	7	10·01
8	5·89	8	6·93	8	7·97	8	9·00	8	10·04
9	5·92	9	6·95	9	7·99	9	9·03	9	10·06
1·0230	5·94	1·0270	6·98	1·0310	8·02	1·0350	9·05	1·0390	10·09
1	5·97	1	7·01	1	8·04	1	9·08	1	10·11
2	6·00	2	7·03	2	8·07	2	9·10	2	10·14
3	6·02	3	7·06	3	8·09	3	9·13	3	10·17
4	6·05	4	7·08	4	8·12	4	9·16	4	10·19
5	6·07	5	7·11	5	8·14	5	9·18	5	10·22
6	6·10	6	7·13	6	8·17	6	9·21	6	10·25
7	6·12	7	7·16	7	8·20	7	9·23	7	10·27
8	6·15	8	7·19	8	8·22	8	9·26	8	10·30
9	6·18	9	7·21	9	8·25	9	9·29	9	10·32

TABLE XXII—*continued*

Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.
1·0400	10·35	1·0440	11·39	1·0480	12·43	1·0520	13·47	1·0560	14·51
1	10·37	1	11·42	1	12·45	1	13·49	1	14·54
2	10·40	2	11·44	2	12·48	2	13·52	2	14·56
3	10·43	3	11·47	3	12·51	3	13·55	3	14·59
4	10·45	4	11·49	4	12·53	4	13·57	4	14·61
5	10·48	5	11·52	5	12·56	5	13·60	5	14·64
6	10·51	6	11·55	6	12·58	6	13·62	6	14·67
7	10·53	7	11·57	7	12·61	7	13·65	7	14·69
8	10·56	8	11·60	8	12·64	8	13·68	8	14·72
9	10·58	9	11·62	9	12·66	9	13·70	9	14·74
1·0410	10·61	1·0450	11·65	1·0490	12·69	1·0530	13·73	1·0570	14·77
1	10·63	1	11·68	1	12·71	1	13·75	1	14·80
2	10·66	2	11·70	2	12·74	2	13·78	2	14·82
3	10·69	3	11·73	3	12·77	3	13·80	3	14·85
4	10·71	4	11·75	4	12·79	4	13·83	4	14·87
5	10·74	5	11·78	5	12·82	5	13·86	5	14·90
6	10·76	6	11·81	6	12·84	6	13·89	6	14·93
7	10·79	7	11·83	7	12·87	7	13·91	7	14·95
8	10·82	8	11·86	8	12·90	8	13·94	8	14·98
9	10·84	9	11·88	9	12·92	9	13·96	9	15·00
1·0420	10·87	1·0460	11·91	1·0500	12·95	1·0540	13·99	1·0580	15·03
1	10·90	1	11·94	1	12·97	1	14·01	1	15·06
2	10·92	2	11·96	2	13·00	2	14·04	2	15·08
3	10·95	3	11·99	3	13·03	3	14·07	3	15·11
4	10·97	4	12·01	4	13·05	4	14·09	4	15·14
5	11·00	5	12·04	5	13·08	5	14·12	5	15·16
6	11·03	6	12·06	6	13·10	6	14·14	6	15·19
7	11·05	7	12·09	7	13·13	7	14·17	7	15·22
8	11·08	8	12·12	8	13·15	8	14·20	8	15·24
9	11·10	9	12·14	9	13·18	9	14·22	9	15·27
1·0430	11·13	1·0470	12·17	1·0510	13·21	1·0550	14·25	1·0590	15·29
1	11·15	1	12·19	1	13·23	1	14·28	1	15·32
2	11·18	2	12·22	2	13·26	2	14·30	2	15·35
3	11·21	3	12·25	3	13·29	3	14·33	3	15·37
4	11·23	4	12·27	4	13·31	4	14·35	4	15·40
5	11·26	5	12·30	5	13·34	5	14·38	5	15·42
6	11·28	6	12·32	6	13·36	6	14·41	6	15·45
7	11·31	7	12·35	7	13·39	7	14·43	7	15·48
8	11·34	8	12·38	8	13·42	8	14·46	8	15·50
9	11·36	9	12·40	9	13·44	9	14·48	9	15·53

TABLE XXII—*continued*

Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.
1·0600	15·55	1·0640	16·60	1·0680	17·64	1·0720	18·69	1·0760	19·73
1	15·58	1	16·62	1	17·67	1	18·71	1	19·76
2	15·61	2	16·65	2	17·69	2	18·74	2	19·79
3	15·63	3	16·68	3	17·72	3	18·76	3	19·81
4	15·66	4	16·70	4	17·75	4	18·79	4	19·84
5	15·68	5	16·73	5	17·77	5	18·82	5	19·86
6	15·71	6	16·75	6	17·80	6	18·84	6	19·89
7	15·74	7	16·78	7	17·83	7	18·87	7	19·92
8	15·76	8	16·80	8	17·85	8	18·90	8	19·94
9	15·79	9	16·83	9	17·88	9	18·92	9	19·97
1·0610	15·81	1·0650	16·86	1·0690	17·90	1·0730	18·95	1·0770	20·00
1	15·84	1	16·88	1	17·93	1	18·97	1	20·02
2	15·87	2	16·91	2	17·95	2	19·00	2	20·05
3	15·89	3	16·94	3	17·98	3	19·03	3	20·07
4	15·92	4	16·96	4	18·01	4	19·05	4	20·10
5	15·94	5	16·99	5	18·03	5	19·08	5	20·12
6	15·97	6	17·01	6	18·06	6	19·10	6	20·15
7	16·00	7	17·04	7	18·08	7	19·13	7	20·18
8	16·02	8	17·07	8	18·11	8	19·16	8	20·20
9	16·04	9	17·09	9	18·14	9	19·18	9	20·23
1·0620	16·07	1·0660	17·12	1·0700	18·16	1·0740	19·21	1·0780	20·26
1	16·10	1	17·14	1	18·19	1	19·23	1	20·28
2	16·13	2	17·17	2	18·22	2	19·26	2	20·31
3	16·15	3	17·20	3	18·24	3	19·29	3	20·34
4	16·18	4	17·22	4	18·27	4	19·31	4	20·36
5	16·21	5	17·25	5	18·30	5	19·34	5	29·39
6	16·23	6	17·27	6	18·32	6	19·37	6	20·41
7	16·26	7	17·30	7	18·35	7	19·39	7	20·44
8	16·28	8	17·33	8	18·37	8	19·42	8	20·47
9	16·31	9	17·35	9	18·40	9	19·44	9	20·49
1·0630	16·33	1·0670	17·38	1·0710	18·43	1·0750	19·47	1·0790	20·52
1	16·36	1	17·41	1	18·45	1	19·50	1	20·55
2	16·39	2	17·43	2	18·48	2	19·52	2	20·57
3	16·41	3	17·46	3	18·50	3	19·55	3	20·60
4	16·44	4	17·48	4	18·53	4	19·58	4	20·62
5	16·47	5	17·51	5	18·56	5	19·60	5	20·65
6	16·49	6	17·54	6	18·58	6	19·63	6	20·68
7	16·52	7	17·56	7	18·61	7	19·65	7	20·70
8	16·54	8	17·59	8	18·63	8	19·68	8	20·73
9	16·57	9	17·62	9	18·66	9	19·71	9	20·75

TABLE XXII—*continued*

Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.
1.0800	20.78	1.0840	21.83	1.0880	22.88	1.0920	23.93	1.0960	24.99
1	20.81	1	21.86	1	22.91	1	23.96	1	25.01
2	20.83	2	21.88	2	22.93	2	23.99	2	25.04
3	20.86	3	21.91	3	22.96	3	24.01	3	25.07
4	20.89	4	21.94	4	22.99	4	24.04	4	25.09
5	20.91	5	21.96	5	23.01	5	24.07	5	25.12
6	20.94	6	21.99	6	23.04	6	24.09	6	25.14
7	20.96	7	22.02	7	23.07	7	24.12	7	25.17
8	20.99	8	22.04	8	23.09	8	24.14	8	25.20
9	21.02	9	22.07	9	23.12	9	24.17	9	25.22
1.0810	21.04	1.0850	22.09	1.0890	23.14	1.0930	24.20	1.0970	25.25
1	21.07	1	22.12	1	23.17	1	24.22	1	25.28
2	21.10	2	22.15	2	23.20	2	24.25	2	25.30
3	21.12	3	22.17	3	23.22	3	24.27	3	25.33
4	21.15	4	22.20	4	23.25	4	24.30	4	25.36
5	21.17	5	22.22	5	23.28	5	24.33	5	25.38
6	21.20	6	22.25	6	23.30	6	24.35	6	25.41
7	21.23	7	22.28	7	23.33	7	24.38	7	25.43
8	21.25	8	22.30	8	23.35	8	24.41	8	25.46
9	21.28	9	22.33	9	23.38	9	24.43	9	25.49
1.0820	21.31	1.0860	22.36	1.0900	23.41	1.0940	24.46	1.0980	25.51
1	21.33	1	22.38	1	23.43	1	24.49	1	25.54
2	21.36	2	22.41	2	23.46	2	24.51	2	25.56
3	21.38	3	22.43	3	23.49	3	24.54	3	25.59
4	21.41	4	22.46	4	23.51	4	24.57	4	25.62
5	21.44	5	22.49	5	23.54	5	24.59	5	25.64
6	21.46	6	22.51	6	23.57	6	24.62	6	25.67
7	21.49	7	22.54	7	23.59	7	24.64	7	25.70
8	21.52	8	22.57	8	23.62	8	24.67	8	25.72
9	21.54	9	22.59	9	23.65	9	24.70	9	25.75
1.0830	21.57	1.0870	22.62	1.0910	23.67	1.0950	24.72	1.0990	25.78
1	21.59	1	22.65	1	23.70	1	24.75	1	25.80
2	21.62	2	22.67	2	23.72	2	24.78	2	25.83
3	21.65	3	22.70	3	23.75	3	24.80	3	25.85
4	21.67	4	22.72	4	23.77	4	24.82	4	25.88
5	21.70	5	22.75	5	23.80	5	24.85	5	25.91
6	21.73	6	22.78	6	23.83	6	24.88	6	25.93
7	21.75	7	22.80	7	23.85	7	24.91	7	25.96
8	21.78	8	22.83	8	23.88	8	24.93	8	25.99
9	21.80	9	22.86	9	23.91	9	24.96	9	26.01

Table XXII—*continued*

Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.	Sp. gr. at 15°/15°.	Grams of Extract in 100 c.c.
1·1000	26·04	1·1030	26·83	1·1060	27·62	1·1090	28·41	1·1120	29·20
1	26·06	1	26·85	1	27·65	1	28·43	1	29·23
2	26·09	2	26·88	2	27·67	2	28·46	2	29·25
3	26·12	3	26·91	3	27·70	3	28·49	3	29·28
4	26·14	4	26·93	4	27·72	4	28·51	4	29·31
5	26·17	5	26·96	5	27·75	5	28·54	5	29·33
6	26·20	6	26·99	6	27·78	6	28·57	6	29·36
7	26·22	7	27·01	7	27·80	7	28·59	7	29·39
8	26·25	8	27·04	8	27·83	8	28·62	8	29·41
9	26·27	9	27·07	9	27·86	9	28·65	9	29·44
1·1010	26·30	1·1040	27·09	1·1070	27·88	1·1100	28·67	1·1130	29·47
1	26·33	1	27·12	1	27·91	1	28·70	1	29·49
2	26·35	2	27·15	2	27·93	2	28·73	2	29·52
3	26·38	3	27·17	3	27·96	3	28·75	3	29·54
4	26·41	4	27·20	4	27·99	4	28·78	4	29·57
5	26·43	5	27·22	5	28·01	5	28·81	5	29·60
6	26·46	6	27·25	6	28·04	6	28·83	6	29·62
7	26·49	7	27·27	7	28·07	7	28·86	7	29·65
8	26·51	8	27·30	8	28·09	8	28·88	8	29·68
9	26·54	9	27·33	9	28·12	9	28·91	9	29·70
1·1020	26·56	1·1050	27·35	1·1080	28·15	1·1110	28·94	1·1140	29·73
1	26·59	1	27·38	1	28·17	1	28·96	1	29·76
2	26·62	2	27·41	2	28·20	2	28·99	2	29·78
3	26·64	3	27·43	3	28·22	3	29·02	3	29·81
4	26·67	4	27·46	4	28·25	4	29·04	4	29·83
5	26·70	5	27·49	5	28·28	5	29·07	5	29·86
6	26·72	6	27·51	6	28·30	6	29·09	6	29·89
7	26·75	7	27·54	7	28·33	7	29·12	7	29·91
8	26·78	8	27·57	8	28·36	8	29·15	8	29·94
9	26·80	9	27·59	9	28·38	9	29·17	9	29·96

If the prescribed conditions are followed exactly, the difference between two determinations does not exceed 0·03–0·04 gr. (0·6–0·8 gram per litre). As a rule, the value of the extract determined directly is somewhat lower than that calculated; for ordinary wines the difference is about 0·8–1·0 gram per litre.

5. Determination of the Ash

The ash of wine contains principally salts of potassium, magnesium, calcium, sodium, aluminium and iron, with carbonic, phosphoric, sulphuric, hydrochloric and silicic acids. It is determined, in one of the two following ways :

(*a*) If the extract has been determined directly, use is made of the dry extract obtained; if not, 50 c.c. of the wine are evaporated to dryness in

a platinum dish, the residue in either case being incinerated. To this end, the residue is first very carefully charred over a tiny flame and the dish then placed in a small cold muffle, which is gradually heated to incipient dark redness. The temperature should not be allowed to go beyond this point, so that fusion of the ash and loss by evaporation may be avoided. In general it is easy to burn the carbon completely, but if this cannot be done the temperature of the muffle need not be raised ; it will suffice to allow the dish to cool, to moisten the carbonaceous residue with water, to evaporate it quite to dryness and to heat again to nascent redness, this treatment being repeated if necessary. When incineration is complete, the dish is allowed to cool in a desiccator, and rapidly weighed.

(b) If the wine contains not more than 30 grams of dry extract per litre, the extract obtained directly may be utilised ; when the extract is greater than this, 50 c.c. of the original wine are evaporated and the ash determined on the residual extract.

In either case the dish with the extract is placed on an asbestos sheet and the drying of the extract commenced over a small flame, care being taken to avoid loss. The dish is subsequently heated directly over a flame, the extract being charred, the mass extracted with water, the aqueous extract filtered through a small ashless filter, all the carbon burnt away, and the aqueous extract and filter added to the same dish.

The whole is evaporated to dryness on a water-bath, dried on asbestos or in an air-oven, heated carefully to dull redness and cooled, the ash being then taken up in a few drops of saturated ammonium carbonate solution, again taken down to dryness, heated to dull redness, cooled in a desiccator and weighed.

6. Determination of the Total Alkalinity of the Ash

The alkalinity is due mainly to potassium carbonate formed by the calcination of the potassium bitartrate.

The ash from the preceding determination is taken up in a little boiling water and transferred completely to a small dish. After addition of two drops of phenolphthalein and 50 c.c. of N/10-hydrochloric acid, the liquid is heated to incipient boiling, which is maintained for 3–5 minutes, with frequent stirring. When the liquid has cooled, the excess of acid is titrated with N/10-caustic soda solution. The alkalinity is expressed in c.c. of N-alkali per litre of wine or as potassium carbonate (c.c. of N-alkali × 0·069).

The values obtained by the procedure here described do not represent exactly the alkalinity of the ash, but are somewhat too low. This is due to the action which the phosphoric acid—present in the wine as primary phosphate—exerts on the alkaline carbonates during incineration It has, therefore, been suggested [1] that the alkalinity of the ash be determined after elimination of the phosphoric acid by precipitation. Such procedure has not, however, been adopted in practice and most of the available data refer to the method described above.

[1] Farnsteiner : *Zeitschr. Unt. Nahr- und Genuss-mittel,* 1907, XIII, p. 305 ; 1908, XVI, p. 629.

7. Determination of the Acidity

The acidity of wine is due to organic acids, some of which are fixed—tartaric, malic, succinic—whilst others, such as acetic and also formic, butyric and propionic, which are found in minimal proportions, are volatile ; carbonic acid plays no part in the acidity of wine.

The acidity of wine is distinguished as *total, volatile* and *fixed*, the last representing the difference between the first two. The determinations are made as follows [1]:

1. Total Acidity.—25 c.c. of the wine are shaken to expel any carbon dioxide present (with sparkling wines gentle heating on a water-bath is necessary) and then titrated with N/4-potassium hydroxide, very sensitive dry litmus paper being used as indicator : multiplication of the number of c.c. of alkali used by 0·750 (or 0·49) gives the total acidity as grams of tartaric (sulphuric) acid per litre of the wine.

2. Volatile Acidity.—This is determined by distilling the wine in a current of steam and estimating the acidity of the distillate as follows :

50 (or 25, if the wine is acid or acetous) c.c. of the wine are diluted with an equal volume of water in a round-bottomed flask holding about 250 c.c. and fitted with a double-bored rubber stopper.

Through the latter pass : (I) A glass tube about 4 mm. wide drawn out at the bottom to 1 mm., this reaching into the liquid and almost to the bottom of the flask ; this tube is connected with a steam generator or a flask fitted with a safety tube containing at least a litre of water ; (2) another tube provided with a safety bulb and connected with a condenser leading to a flask of about 300 c.c. capacity with a mark at 200 c.c.

The wine is first distilled without steam until the volume is reduced to 25 c.c., when the steam is turned on (not at too great a pressure, since otherwise the liquid may be forced over), the distillation being regulated so that the volume of liquid in the flask is kept practically constant at 25 c.c.

The distillation is stopped when 200 c.c. of distillate have been obtained, this requiring about 45 minutes. The distillate is titrated with N/10-alkali in presence of phenolphthalein.[2]

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[1] A new method has recently been introduced of regarding the acidity of wine, the latter being expressed in terms of the quantity or concentration of the hydrogen ions present. As is well known, the amount of these ions depends on the nature of the acids, which are stronger the more capable they are of dissociating when brought into solution. For determining the concentration of the hydrogen ions of wine, or the *acid energy*, the method most commonly used at the present time is based on the velocity of inversion of saccharose by the acids of the wine. It is carried out at a temperature of 76°—obtained by means of a boiling carbon tetrachloride bath—after the destruction of the invertase. The wine, in which a given quantity of saccharose is dissolved, is brought to the above temperature and from the amount of saccharose inverted in a given time an inversion constant is calculated, which represents the acid energy of the wine. The data obtained up to the present are limited to a few wines and it is not yet possible to deduce any conclusions of a general character. For fuller information, special publications should be consulted : Quartaroli : *Staz. sper. agr. Ital.*, 1910, p. 87 ; 1912, p. 90 ; Dutoit and Duboux : *Analyse des Vins par volumetrie physico-chimique*, Lausanne, 1912 ; Mensio and Garino : *Ann. d. R. Acc. d'Agric. di Torino*, Vol. LVI.

[2] Neutralisation is just reached when a drop of the alkali gives a distinctly pink coloration which persists for a few moments. This coloration disappears after some time owing to hydrolysis of the esters of the wine which pass over into the distillate.

The volatile acidity is expressed as grams of acetic acid per litre, the number of c.c. of N/10-alkali being multiplied by 0·120 (or 0·240) if 50 (or 25) c.c. of the wine were taken.

3. Fixed Acidity.—This is determined by difference. The volatile acidity is multiplied by 1·25 to refer it to tartaric acid, the number thus obtained being subtracted from the total acidity calculated as in (1) ; the remainder represents the fixed acidity in grams of tartaric acid per litre.

The acidity of a wine bears a certain relation to its alcoholic strength, diminishing as the latter increases. On this basis Halphen and Gautier have established rules for the detection of the *watering* of wine. The methods of applying these rules are given below. As regards Italian wines it must, however, be pointed out that, although these rules furnish sound indications for most of such wines, yet they do not seem to apply to the wines of certain special districts.

(a) *Halphen's rule* (*acid : alcohol ratio*).

To apply this rule, the alcoholic strength (by volume) and the fixed acidity of the wine are determined. The latter, expressed as sulphuric acid, is increased by 0·7 (this corresponding with the maximum value of the volatile acidity in ordinary normal wines), and the value thus obtained divided by the alcoholic strength ; the quotient is the ratio sought.

This ratio is compared with that established experimentally by Halphen for wine of the same alcoholic strength. Halphen's values are expressed by the formula :

$$x = 1·160 - 0·07 y,$$

y being the alcoholic strength of the wine.

If the ratio found is less than that calculated by the above expression, watering may be suspected.

For *Italian wines*, Possetto and Issoglio give the following values of the Halphen ratio :

Alcoholic Strength.	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
15	0·110	—	—	—	—	—	—	—	—	—
14	0·180	0·173	0·166	0·159	0·152	0·145	0·138	0·131	0·124	0·117
13	0·250	0·243	0·236	0·229	0·222	0·215	0·208	0·201	0·194	0·187
12	0·320	0·313	0·306	0·299	0·292	0·285	0·278	0·271	0·264	0·257
11	0·390	0·383	0·376	0·369	0·362	0·355	0·348	0·341	0·334	0·327
10	0·460	0·453	0·446	0·439	0·432	0·425	0·418	0·411	0·404	0·397
9	0·530	0·523	0·516	0·509	0·502	0·495	0·488	0·481	0·474	0·467
8	0·600	0·593	0·586	0·579	0·572	0·565	0·558	0·551	0·544	0·537
7	0·670	0·663	0·656	0·649	0·642	0·635	0·628	0·621	0·614	0·607
6	0·740	0·733	0·726	0·719	0·712	0·705	0·698	0·691	0·684	0·677
5	0·810	0·803	0·796	0·789	0·782	0·775	0·768	0·761	0·754	0·747
4	0·880	0·873	0·866	0·859	0·852	0·845	0·838	0·831	0·824	0·817
3	0·950	0·943	0·936	0·929	0·922	0·915	0·908	0·901	0·894	0·887

If the value found for the wine is above that given in this table, the wine is normal, but if it is lower, addition of water is suspected ; when the deficit is 0·120, or even 0·100, these two authors regard watering as proved.

EXAMPLES : (1) Alcoholic degree, 10 ; fixed acidity, as sulphuric acid per litre, 3·96. (3·96 + 0·7) ÷ 10 = 0·466. Value from table, 0·460 ; wine consequently regarded as normal.

(2) Alcoholic strength, 9 ; fixed acidity, 3·35. $(3·35 + 0·7) \div 9 = 0·472$. Value from table, 0·530. Addition of water consequently suspected.

(3) Alcoholic strength, 8 ; fixed acidity, 2·98. $(2·98 + 0·7) \div 8 = 0·460$. Value from table 0·6co. Watering regarded as proved.

(b) *Gautier's rule* (sum of alcohol and acidity).

This rule is applied as follows : To the total amount of alcohol [1] in 100 c.c. of the wine are added the fixed acidity per litre expressed as sulphuric acid and one-tenth of the volatile acidity, also as sulphuric acid per litre.

From this sum are deducted :

1. The quantity of extraneous acids added to the wine, expressed as sulphuric acid per litre.

2. The quantity of alcohol which may be assumed to be derived from alcoholisation of the wine calculated as described later (*see* Determination of Glycerine).

3. The value 0·20 for every gram of potassium sulphate exceeding 2 grams.

According to Gautier, the value of the sum, alcohol + acidity, varies between 13 and 17, a value below 12·5 indicating addition of water.

EXAMPLES : (1) An ordinary dry wine had an alcoholic strength 10, while total acidity plus one-tenth of the volatile acidity per litre (as sulphuric acid) is 4·20. Since $10 + 4·20 = 14·20$, which exceeds 12·5, the wine is regarded as normal.

(2) Percentage of alcohol, 8 and acidity 3·36 ; $8 + 3·36 = 11·36$, which is less than 12·5, so that the wine is watered.

8. Determination of the Total Tartaric Acid

This is precipitated as potassium bitartrate by addition of excess of a potassium salt and the solution then titrated with N/4-alkali.

100 c.c. of the wine are treated in a beaker with 2 c.c. of glacial acetic acid, 0·5 c.c. of 20% potassium acetate solution and 20 grams of pure, powdered potassium chloride. The latter is dissolved by protracted shaking and 20 c.c. of 95% alcohol then added. The liquid is shaken further and the precipitation of the potassium bitartrate assisted by energetic rubbing of the walls of the beaker with the end of a glass rod. After a stand of 15 hours at about 15°, the liquid is filtered through a Gooch crucible charged with asbestos, the liquid being poured on when the pump is in action. The beaker is washed two or three times with a few c.c. of a solution of 15 grams of potassium chloride in 25 c.c. of 95% alcohol and 90 c.c. of water, the crystalline precipitate and the crucible being washed with the same solution, of which 20 c.c. altogether are used ; for this purpose a test-tube is fitted as a wash-bottle.

The crucible is washed externally and placed in a beaker of hot water, the precipitate being completely dissolved by removing the crucible and washing it with a jet of hot water. The liquid is then titrated in the hot with N/4-caustic soda, litmus paper being used as indicator.

The number of c.c. used is increased by 0·6 to correct for the solubility of the bitartrate in the reagents used and the sum multiplied by 0·375 to obtain the grams of total tartaric acid per litre.

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[1] The total alcohol is given by the sum of the alcohol present in the wine and of that which would be produced by fermentation of the sugar still present ; the latter amount of alcohol is calculated by multiplying the percentage of sugar by 0·55.

9. Determination of the Sugars

The object of this determination, which is carried out principally with sweet wines, is to estimate the reducing sugars and any saccharose which may have been added to the wine. Both the optical and chemical methods are used (*see also* Sugars, General Methods). The polarimetric method is also sometimes used with sweet wines in order to ascertain if dextrin or commercial glucose has been added (*see* later, p. 196).

1. Preparation of the Solutions : Polarimetric Tests.—100 c.c. of the wine are neutralised in a porcelain dish with caustic potash solution, care being taken not to render the liquid alkaline.[1] The alcohol is evaporated off on a water-bath and the residue introduced into a 200 c.c. flask, into which also the dish is rinsed several times with water. A slight excess (about 5 c.c.) of basic lead acetate solution is added, the precipitate formed being allowed to settle and sufficient saturated sodium sulphate solution added, drop by drop, to precipitate the excess of lead. When further addition of the sodium sulphate solution fails to produce a precipitate, the liquid is made up to 200 c.c. with water, shaken, allowed to settle and filtered by decantation through a dry filter.

Part of the filtrate serves directly for saccharimetric reading and for the determination of the reducing sugars by means of Fehling's solution (*see* later), while another part is *inverted*. For this purpose 50 c.c. of the filtrate are heated in a 100 c.c. flask with 5 c.c. of hydrochloric acid (sp. gr. 1·10) for a quarter of an hour in a water-bath at 68–70° ; the liquid is then cooled rapidly, neutralised with caustic soda (best with a solution standarised with respect to the hydrochloric acid of sp. gr. 1·10), made up to volume and filtered, if necessary, through a dry filter.

The readings of the non-inverted and inverted solutions in the Ventzke scale saccharimeter are multiplied by 2 and 4 respectively in order to obtain the polarisations P and P_1 of the undiluted wine before and after inversion.[2]

If these polarisations are equal, saccharose is not present, and in this case the reducing sugars are determined as in 2.

If, however, P_1 is below P, the wine contains saccharose, which is calculated as indicated in 3 (below).

2. Determination of the Reducing Sugars.—This determination is made volumetrically with Fehling's solution, 10 c.c. of the latter, diluted with 40 c.c. of water being used for each test.

The determination is made on the uninverted liquid prepared as described above and diluted, if necessary, to give a solution containing not more than 1% of reducing sugars (0·5–1%), so that 5–10 c.c. will be required to reduce completely the above quantity of Fehling's solution.

The necessary dilution may easily be deduced (if saccharose is not present) from the percentage of extract present in the wine, since this, diminished by 2, gives approximately the percentage of reducing sugars ;

[1] Since even a small excess of alkali may produce decomposition of the sugar, it is well, after exact neutralisation, to add a drop of dilute acetic acid ; the very faint acid reaction thus produced has no effect on any saccharose which may be present.

[2] The formulæ given below in which the polarisations occur refer to vessels graduated in Mohr c.c.

it must further be remembered that, in the preparation of the liquid, the wine has been diluted to double its volume. If the extract has not been determined, a preliminary test is made by adding to boiling Fehling's solution, drop by drop from a graduated pipette, the filtered saccharine liquid prepared as described above. The addition is continued and the boiling maintained until the cuprous oxide formed assumes a bright colour readily distinguished with practice. This point represents the completion of the precipitation and may be checked by filtering a few drops of the boiling liquid, acidifying with acetic acid and testing with potassium ferrocyanide. The quantity of the saccharine liquid used in this preliminary test indicates how many times the liquid must be diluted to give a solution suitable for the determination.

This dilution is effected by running the necessary volume of the saccharine liquid from a burette into a 100 c.c. flask and making up to the mark with water. The liquid thus diluted is placed in a burette and various tests made with Fehling's solution and with different volumes of the liquid, as already described (*see* Sugars, General Methods), until with two quantities of the liquid differing by 0·1 c.c., in one case only is a trace of copper detectable in the filtrate.

The mean of these two last determinations gives the volume a c.c. of the diluted saccharine liquid necessary to reduce completely 10 c.c. of Fehling's solution diluted with 40 c.c. of water. If n represents the number of volumes of dilute saccharine liquid obtained from 1 vol. of wine, the reducing sugars g per litre of wine, calculated as invert sugar, are given by the formula :

$$g = \frac{51 \cdot 5 \, n}{a}.$$

To ascertain if the reducing sugars found contain excess of levulose or of glucose, the theoretical polarisation, on the assumption that the reducing sugars consist of invert sugar, may be calculated by means of the formula :

$$x = -\frac{g \, (42 \cdot 66 - 0 \cdot 5 \, t)}{274 \cdot 19},$$

where g is the quantity of reducing sugar per litre and t the temperature at which the polarisation is determined. If the polarisation found, P, is greater—or more dextro-rotatory—than the calculated value, there is excess of dextrose ; but if less—or more lævo-rotatory—there is excess of levulose.

The respective quantities of levulose l and glucose d per litre may also be calculated by the formulæ :

$$l = \frac{10 \, (0 \cdot 3048 \, g - P)}{9 \cdot 278 - 0 \cdot 04 \, t}$$

$$d = g - l,$$

where P is the polarisation (with the proper sign) of the undiluted wine.

For the application of these formulæ in the case when saccharose is present, *see* later, 3.

In general, normal wines contain slightly more levulose than dextrose, the latter being the more readily acted on during fermentation. The opposite case may occur in genuine wines, but often results from addition of glucose or dextrin (*see below*, 10).

3. Determination of the Saccharose.—The quantity s of saccharose per litre is calculated by means of Clerget's formula :

$$s = 10 \ \frac{26 \cdot 048 \ (P - P_1)}{142 \cdot 66 - 0 \cdot 5 \ t},$$

where P and P_1 are the polarisations (with the proper signs) of the undiluted wine before and after inversion determined as indicated above, 1.

The value of s may be checked by determining the reducing sugars in the inverted solution with Fehling's solution, as in 2 (above), the difference between the reducing sugars before and after inversion being multiplied by 0·95.

When saccharose is present, the occurrence of levulose or glucose in excess is ascertained by calculating the theoretical polarisation for the inverted liquid and comparing it with the polarisation P_1 found after inversion. Further, to determine the quantities of glucose and levulose composing the reducing sugars, the formulæ given above (2) are applied to the results obtained with the inverted liquid. Since, however, the quantities thus calculated include the glucose and levulose formed by the inversion of the saccharose, the amounts of pre-existing glucose and levulose are deduced by subtracting from each of the values found the amount of the saccharose, s, divided by 1·90.

10. Detection of Dextrin and of Impure Glucose

Wine may contain dextrin and other unfermentable substances (iso-maltose, etc.) in consequence either of the addition of commercial glucose, which contains such substances as impurities, or of their direct addition with the object of increasing the extract. Their detection is carried out as follows :

(*a*) If the wine contains, at the most, 1 gram of reducing sugar per litre and is lævo-rotatory or inactive or has a dextro-rotation not exceeding + 0·8 saccharimetric divisions (+ 0·3 circular degrees), it has suffered no admixture with impure glucose.

(*b*) If the wine contains more than 1 gram of reducing sugar per litre and has a rotation between + 0·8 and + 1·7 saccharimetric divisions, it is probable that it contains dextrin and other unfermentable but optically active substances which accompany glucose.

(*c*) If the wine contains more than 1 gram of reducing sugar per litre and exhibits a rotation exceeding + 1·7 divisions, *dextrin* is tested for as follows :

100 c.c. of the wine are evaporated to 5 c.c. and the residue treated, with shaking, with 90% alcohol until no further precipitate is formed. After 2 hours the liquid is filtered, the precipitate being dissolved in 30 c.c. of water and the solution introduced into a 100 c.c. flask, together with

1 c.c. of hydrochloric acid (D 1·12). The flask is closed with a stopper traversed by a glass tube a metre long and is immersed in a boiling water-bath for 3 hours; the liquid is then neutralised with soda, made up to 100 c.c. and tested with Fehling's solution. Any reduction indicates the presence of dextrin, since those bodies present in natural wines which are precipitable by 90% alcohol do not yield sugars when heated with hydrochloric acid.

The *impurities* which accompany the glucose are tested for as follows:

A volume of 210 c.c. of the wine is evaporated to one-third of its bulk, the residue being taken up in sufficient water to give a solution containing about 15% of sugar and the solution placed in a flask and seeded with a little fresh, optically inactive yeast. Fermentation is allowed to proceed at 20–25° C.

The fermented liquid is treated with a few drops of 20% potassium acetate solution and evaporated in a porcelain dish on a water-bath to a dense syrup. The latter is shaken with 200 c.c. of 90% alcohol, the liquid being filtered and the residue and the filter washed with 90% alcohol. Most of the alcohol is distilled off and the remainder evaporated, the residue being made up with water to 10 c.c., well mixed with 2–3 grams of pure animal charcoal and filtered into a small cylinder. The solid residue is washed with small proportions of boiling water until the total volume, cooled to 15° C., amounts to 30 c.c. If this liquid gives a rotation greater than + 1·4 saccharimetric divisions, the wine contains starch glucose. If the rotation is + 1·4, or slightly less, the charcoal is again washed with hot water until a further 30 c.c. of filtrate is obtained, any rotation this liquid shows being added to the previous one. If the second rotation is as much as one-fifth of the first, a third washing of the charcoal becomes necessary.

11. Determination of the Glycerine

The procedure here varies according as ordinary wine containing little sugar or sweet wine is concerned.

1. Ordinary Wine (containing not more than 2% of sugar).—100 c.c. of the wine are evaporated to about 10 c.c. in a round-bottomed porcelain dish on a water-bath. 5 grams of quartz sand (not too fine) are then added and milk of lime, prepared with 40% of calcium hydroxide, until the reaction is strongly alkaline, the evaporation being continued until a soft paste, capable of easy manipulation with a glass rod, is obtained. The residue is heated on the water-bath with 50 c.c. of 96% alcohol, the whole being mixed with a glass rod until a homogeneous paste is obtained; the forma-tion of solid crusts should be avoided as far as possible. The liquid is then filtered through a pleated filter into a flask and the dish and filter washed several times with 96% alcohol, of which about 150 c.c. in all should be used. A few pieces of pumice are added to prevent bumping and the flask connected with a condenser and the alcohol distilled off until about 10 c.c. of liquid remain. The condenser is then removed, the remainder of the alcohol expelled on the water-bath and the cold, syrupy residue dissolved in 10 c.c. of absolute alcohol; 15 c.c. of anhydrous ether are then added,

the precipitate formed being allowed to settle and the clear ethereal-alcoholic liquid filtered through a small filter into a tared wide-mouthed weighing-bottle with a ground stopper. The flask and the filter are subsequently washed with two or three small quantities of a mixture of 2 volumes of absolute alcohol with 3 volumes of anhydrous ether.

The weighing bottle is then placed on a hot water-bath and the solvent evaporated below its boiling point. The bottle is dried in a steam-oven for an hour, closed, allowed to cool in a desiccator and weighed. The increase in weight, multiplied by 10, gives the amount of glycerine per litre of the wine.

2. Sweet Wine.—The following method, devised by G. Fabris,[1] is used : 50 c.c. of the wine are well mixed in a round-bottomed porcelain dish with about 5 grams of siliceous sand (not too fine) and 6–10 grams of very fine, sieved, slaked lime [2] by means of a glass rod. The dish is placed on a water-bath to evaporate the liquid, the mass being frequently stirred, especially when it becomes very thick. The evaporation should then be carefully watched and should be suspended when the contents of the dish assume the consistency of a soft paste still easily miscible with the glass rod, with which also the drier parts adherent to the walls of the vessel should be readily detached ; this stage is usually reached after about two hours' heating. The dish is then withdrawn from the water-bath and about 30 c.c. of hot 96% alcohol added. By means of an iron spatula the solid portions adhering to the rod and to the walls of the capsule are completely removed and the whole thoroughly pounded with the alcohol with a pestle, the coagulum formed during the addition of the alcohol being triturated as much and as carefully as possible. The pestle and the spatula are washed with 96% alcohol (30–40 c.c.) and the dish heated again on the water-bath, the contents being stirred with the rod until the alcohol just begins to boil ; ebullition must, however, be avoided as it might easily lead to loss of liquid. The hot liquid is placed on a dry filter and the insoluble part washed two or three times by decantation with hot 96% alcohol, care being taken to keep the funnel covered with a clock-glass and not to add fresh liquid before the preceding quantity has completely drained away. If the solid part does not seem sufficiently powdered, it is again pounded with the pestle and then poured on to the filter, where it is washed repeatedly with hot 96% alcohol until the volume of the filtrate is about 200 c.c.

The alcoholic liquid, which should be collected in a conical flask of about 300 c.c. capacity, is gently distilled on a water-bath, a few pieces of pumice being added to prevent bumping. The flask is subsequently left open on the water-bath until the little remaining liquid becomes syrupy. When cold the residue is treated, little by little and with shaking, first with 10 c.c. of absolute alcohol and then with 15 c.c. of anhydrous ether. The flask is then corked and the liquid left until it becomes clear and then filtered through a small dry filter into a tared cylindrical weighing-bottle about 6 cm. high and 4 cm. wide and fitted with a ground stopper. The dish and

[1] *Ann. Labor. chim. centrale Gabelle*, 1897, III, p. 225.
[2] The amount of lime to be added should be about equal to that of the sugars contained in the 50 c.c. of wine.
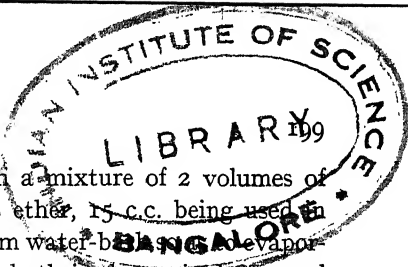
the filter are washed three or four times with a mixture of 2 volumes of absolute alcohol and 3 volumes of anhydrous ether, 15 c.c. being used in all. The bottle is placed on a scarcely lukewarm water-bath to evaporate the ether slowly; the temperature of the bath is then raised to expel the alcohol, but not to make it boil. Finally, the bottle with the syrupy residue is kept in a steam-oven for an hour, allowed to cool in a desiccator and weighed. The weight found, multiplied by 20, gives the glycerine per litre of the wine.[1]

If the amount of glycerine found exceeds 0·5%, it is well to repeat the determination with a smaller quantity, say 25 c.c., of the wine.

The determination of the glycerine is sometimes of importance in deciding if a wine has been " fortified " by addition of alcohol. It is known that the normal alcoholic fermentation of the sugars of wine yields, besides alcohol, also a proportional quantity of glycerine. This quantity varies from a minimum of 7 to a maximum of 14 grams per 100 grams of alcohol. Thus, introduction of the value of a, the grams of alcohol per 100 c.c., and of g, the grams of glycerine per litre of a wine, into the formula:

$$x = \frac{100 \, g}{10 \, a},$$

gives the *ratio x between the glycerine and alcohol*, which should be higher than 7 with wine to which no alcohol has been added.

The minimum percentage of alcohol added by weight, y, may be calculated by means of the formula:

$$y = A - \frac{10 \, G}{7},$$

where A is the number of grams of alcohol in 100 c.c. of the wine and G the grams of glycerine per litre. This formula gives, as is stated, the minimum value for the added alcohol, being based on the minimal ratio between glycerine and alcohol, i.e., 7 : 100. It is, however, evident that a limited proportion of alcohol might be added to a wine with a glycerine : alcohol ratio of 9 without being detectable in this way.

EXAMPLE : A wine contains 8 grams of alcohol per 100 c.c. and 6·68 grams of glycerine per litre. The glycerine-alcohol ratio will be:

$$\frac{100 \times 6·68}{8 \times 10} = 8·3,$$

which, being greater than 7, indicates absence of added alcohol.

The same wine, after addition of alcohol, contains 10·5 grams of alcohol per 100 c.c., whilst the glycerine has remained almost unchanged at 6·6 grams per litre. The glycerine-alcohol ratio is now:

$$x = \frac{100 \times 6·6}{10·5 \times 10} = 5·4,$$

which is less than 7 and indicates fortification.

12. Determination of the Depth of Colour

This is carried out especially with red wines, principally " vins de coupage." Use is made either of Salleron's wine-colorimeter, which gives both the intensity and the character of the colour, or of some other colorimeter,

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[1] If the weighed glycerine is again treated with alcohol and ether, filtered and evaporated as described above, the same weight of glycerine should be obtained.

such as Duboscq's, in which comparison is made either with a typical wine or with an artificial coloured solution.

1. I. Salleron's Wine-colorimeter.—This apparatus (Fig. 51) consists of a stand on which are fixed (1) ten discs of silk, the colours of these varying gradually from violet-red to red, and (2) ten perfectly white discs. Along this stand runs an apparatus carrying two tubes, *A* and *B*, inclined at 45° and corresponding exactly with the series of coloured and white discs respectively. *B* is arranged so that the thickness of a layer of coloured liquid placed therein can be adjusted and measured exactly.
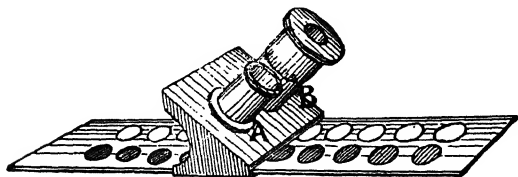
FIG. 51

Salleron takes as unit a wine which, in a layer 3 mm. deep, exhibits an intensity of colour equal to that of one of the tints of his wine-colorimeter scale. Thus, a wine which in this apparatus requires a thickness of 1·5 mm. would have a depth of colour double that of the unit.

The colorimetric observations should not be made in artificial light.

2. Duboscq's Colorimeter.—This consists (Fig. 52) of two glass vessels into each of which a glass cylinder may be lowered by means of a rack and pinion. Light reflected from a mirror underneath passes along the axes of the two vessels and cylinders into a system of two prisms, by means of which the two halves of the field of the eye-piece at the top are illuminated.

The two liquids to be compared are placed in the two vessels and the glass cylinders adjusted until the two halves of the field appear equally illuminated; the respective depths of colour of the two liquids are then inversely proportional to the thicknesses of the layers. Three observations should be made with varying depths of the two liquids and the mean of the three results taken. In the case of wine, a 0·1% solution of Bordeaux red is used as comparison liquid.
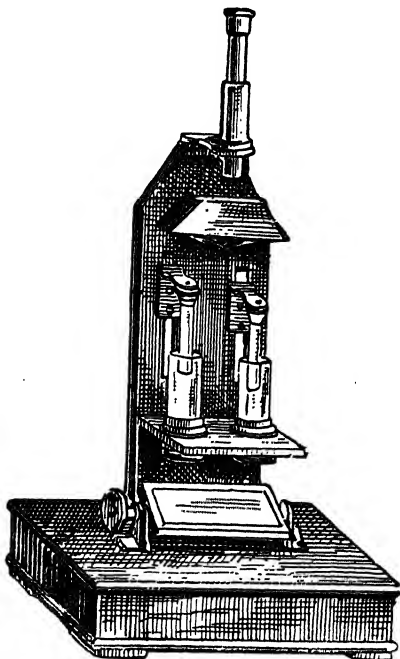
FIG. 52

13. Detection of Extraneous Colouring Matters

1. In Red Wines.—These may be coloured with artificial organic colours (usually mixtures, such as vinolin) or with vegetable colours.

(a) TESTS FOR ARTIFICIAL ORGANIC COLOURS. Use is made of Arata's test, which is that most commonly employed, and of Girard's and König's tests.[1] Arata's test serves for the detection of all artificial organic colouring matters of acid character, Girard's method for that of basic and some acid compounds, and König's for that of basic derivatives.[2]

1. *Arata's method*. 100 c.c. of the wine are gently boiled in a flask to about one-third of its volume, 2-4 c.c. of 10% hydrochloric acid and about half a gram of carefully defatted (with ether) white embroidery wool being then added and the boiling continued for 5 minutes.

The flask is withdrawn from the flame and the liquid poured off, the wool being repeatedly washed with cold water in the same vessel and then boiled for 5 minutes with 100 c.c. of water acidified with hydrochloric acid. The latter is then decanted off and the treatment repeated until a water remaining colourless on boiling is obtained.

The wool is next washed repeatedly with cold distilled water to eliminate the acid liquid and subsequently boiled gently for about 10 minutes with about 50 c.c. of water and 10 drops of ammonia solution (D 0·910) to dissolve any artificial colouring matter fixed by the wool.

The alkaline liquid is decanted into another flask, diluted with an equal amount of water and boiled until it ceases to smell of ammonia; it is then allowed to cool somewhat, and sufficient hydrochloric acid added drop by drop to render the liquid distinctly acid, excess being avoided. A thread of defatted wool, 10–15 cm. long, is then placed in the liquid and the latter boiled for about 5 minutes.

If the wool thus obtained, after thorough washing with cold water, is coloured distinctly red, the conclusion may be drawn that the wine was coloured artificially with an organic dye of acid character, i.e., with a sulphonated azo- or fuchsine derivative (vinolin, Bordeaux red, etc.).

If, however, the coloration is feeble or uncertain, the woollen thread is treated with 50 c.c. of water and 10 drops of ammonia (D 0·910), the colour being refixed, by the exact procedure described above, on a fresh woollen thread 6–8 cm. long. If this third fixation yields even a feeble pink coloration, the presence of artificial organic colouring matter is indicated with certainty.

Sometimes, especially with intensely coloured natural wines, the second or third woollen thread assumes a brownish-yellow coloration, which should be neglected.

2. *Girard's test*. 50 c.c. of the wine are neutralised with 10% ammonia (D 0·960), a further quantity of 5 c.c. of the same ammonia solution being added and the liquid poured into a separating cylinder of about 100 c.c. capacity. 15 c.c. of amyl alcohol are added and the whole shaken slowly, to avoid emulsification, for about 10 minutes. After settling, the liquid below the amyl alcohol is run off and the alcoholic liquid washed three times with water (100 c.c. in all), filtered through a small dry filter and

[1] If identification of the separate colouring matters is desired, the methods described later in the chapter dealing with colouring matters may be employed.

[2] With lapse of time, sometimes after a few months, certain artificial colouring matters undergo modifications and chemical decompositions by which they are decolorised or precipitated; they cannot then be traced directly in wine.

acidified with acetic acid. If the wine contains soluble, artificial, organic colouring matter, the amyl alcohol, either before or after acidification, will be coloured distinctly red, orange-red or pink. Here, too, no notice should be taken of faint yellow or greenish-yellow colorations, which may be obtained with some highly coloured natural wines.

3. König's test. 50 c.c. of the wine are neutralised with 10% ammonia (D 0·960), an excess of 5 c.c. of the same ammonia being added and the liquid boiled gently with about 0·5 gram of defatted white wool until the alcohol and excess of ammonia are expelled. The wool is thoroughly washed with water and heated in a test-tube in a water-bath with 10 c.c. of 10% caustic potash solution until the wool is dissolved.

When cold, the brown liquid is carefully shaken in a separator with one-half its volume of ether for about 5 minutes. After standing, the ethereal layer is separated, filtered through a dry filter and acidified with acetic acid.

If the wine is genuine, the ether remains colourless even after addition of acetic acid; coloration of the ether before or after acidification indicates the presence in the wine of artificial organic colouring matters of basic character (fuchsine, etc.).

(*b*) DETECTION OF VEGETABLE COLOURING MATTERS. Proof of the presence of these substances presents special difficulties owing to their analogy with those naturally contained in wine. The various methods proposed give useful conclusions only when comparison tests are made both on a genuine wine of the same type as that under examination and on the same genuine wine to which the vegetable colouring matter presumed to be present has been added.[1]

2. In White Wines.—White wines may be coloured artificially with caramel or artificial organic dyes (substitutes for caramel, caramelin). The latter are detected as in red wines; in this connection it should be borne in mind that the yellow colours usually added to wines do not consist of individual colouring matters but are mixtures of a yellow material with a brown, a red or, sometimes, a blue compound.

Caramel is detected as follows :

(*a*) *By means of paraldehyde.* 10 c.c. of the wine, 30–50 c.c. of paraldehyde (according to the depth of colour) and 15–20 c.c. of absolute alcohol are repeatedly shaken in a tall, narrow test-glass with a ground stopper so that the liquids mix completely. If the wine does not contain caramel, a white precipitate forms on standing; in the opposite case, the adherent precipitate formed during the course of 24 hours is yellowish-brown or dark-brown according to the amount of the extraneous colouring matter. The supernatant liquid is decanted off and the precipitate washed with absolute alcohol (to eliminate the paraldehyde), dissolved in a little hot water and filtered. The filtrate is evaporated to 1 c.c. [2] and then poured gradually into a fresh solution of phenylhydrazine hydrochloride (2 parts

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[1] For these methods reference may be made to the following publications: Possetto : *La chimica del vino*; M. A. Gautier : *La Sophistication des vins*; Ch. Girard et Sangle-Ferrière : *Analyse des matières alimentaires*; J. Bellier : *Ann. de chim. analyt.*, 1900, p. 407.

[2] From the colour of the filtrate the amount of caramel added may be judged.

of phenylhydrazine hydrochloride, 3 parts of sodium acetate and 20 parts of water). No precipitate forms if the wine is pure, whilst if it contains caramel there is formed, even in the cold, but better after heating on a water-bath for a very short time, a white precipitate which is deposited completely after 24 hours [1] as an amorphous mass (soluble in hot ammonia and reprecipitable by dilute hydrochloric acid).

If the wine contains small quantities of caramel, it is advisable, before treating it with paraldehyde, to concentrate it to one-half or one-third of its volume over sulphuric acid in a vacuum, but *heat should not be applied*. Further, in presence of marked quantities of sugars, it is necessary, before the treatment with phenylhydrazine hydrochloride, to redissolve and reprecipitate with paraldehyde the precipitate obtained with the latter, the bulk of the sugars being thus eliminated.

It should be noted that genuine wines may give a precipitate as a result of the treatment with paraldehyde, but such precipitate is white and is not precipitated from its aqueous solution by phenylhydrazine.

(b) *By means of albumin.* 10 c.c. of the wine are treated with 1 c.c. of albumin solution, prepared by filtering fresh white of egg through thick white woollen and diluting the filtrate with an equal volume of 15% aqueous alcohol solution. Genuine wine gives a marked turbidity caused by the precipitation of the colouring matter of the wine and the filtrate is sensibly less coloured than the wine. If, however, a white wine with considerable colour produces no or scarcely any turbidity and the filtrate is not appreciably less coloured, the addition of caramel may be suspected.

In doubtful cases, check experiments with a genuine wine to which caramel has been added should be made.

14. Determination of the Sulphates

This determination may be made to ascertain if the wine is plastered beyond the allowable limits or to determine the quantity of sulphates present.

1. Determination of the Extent of Plastering.—In Italy plastering of ordinary wine for consumption is allowed to an amount corresponding with 2 grams of potassium sulphate per litre. To ascertain if this limit has been exceeded, use is made of a barium chloride solution able to precipitate such amount of sulphate from an equal volume of wine.

Reagent. 2·6 grams of pure crystallised barium chloride ($BaCl_2 + 2H_2O$) are dissolved in water, mixed with 50 c.c. of hydrochloric acid (D 1·1) and made up to a litre.

Procedure. 50 c.c. of the wine are boiled, 50 c.c. of the reagent run in from a burette and the liquid again boiled, the precipitate being allowed to settle and the liquid filtered. If addition of a few drops of the barium solution to part of the filtrate produces turbidity, the plastering exceeds 0·2% ; if no turbidity is thus produced, while another part of the filtrate

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[1] During this time it is useful to cover the liquid with a layer of 2 c.c. of ether and to invert the tube gently several times ; the ether completely dissolves the reddish-brown resinous products formed and so prevents these from hindering the observation.

gives a precipitate with a drop of dilute sulphuric acid, the plastering is below 0·2%.

2. Determination of the Total Sulphates.

(a) An approximate determination may be made by means of the barium chloride solution prepared for determining the extent of plastering. To this end, separate quantities of 50 c.c. of the wine are treated with different volumes of the barium solution until a filtrate is obtained which remains almost clear with a drop of either the barium solution or dilute sulphuric acid; the amount of the reagent used gives approximately the quantity of sulphates present.

(b) 100 c.c. of the wine, acidified with 5 c.c. of dilute hydrochloric acid, are heated to boiling in a beaker and treated drop by drop with a very hot 10% barium chloride solution until precipitate no longer forms.[1] The liquid is carefully boiled for a few minutes and the covered beaker then left for about 6 hours on a steam-bath. A drop of the barium solution is then added to the perfectly clear liquid to make sure that the precipitation is complete, the hot liquid being decanted on to a filter and the precipitate washed repeatedly by decantation with boiling water containing 10% of alcohol and slightly acidified with hydrochloric acid. The precipitate is finally transferred to the filter and the washing continued until a drop of the filtrate leaves no residue when evaporated on a watch-glass; the funnel is then left in an oven at 100° until the bulk of the water is expelled.

While still moist the filter is placed in a platinum crucible and carefully incinerated and calcined at a dull red heat (not in a blowpipe flame), the crucible being inclined to facilitate access of the air. After being cooled in a desiccator, the crucible is weighed: $BaSO_4 \times 0·7468 = K_2SO_4$.

When the wine contains a marked quantity of sulphurous anhydride, this should first be eliminated by boiling the strongly acidified wine (with HCl) for some time in an atmosphere of carbon dioxide.

15. Determination of the Chlorides

This determination may be made either to ascertain if the wine is salted beyond the permitted extent or to find the quantity of chlorides present.

1. Extent of Salting.—In ordinary wines the chlorides present should not correspond with more than 1 gram of sodium chloride per litre. To ascertain if this limit has been exceeded a silver nitrate solution is prepared capable of precipitating this amount of chlorides from a given quantity of wine.

Reagent. 14·53 grams of pure fused silver nitrate are dissolved to 1 litre.[2]

Procedure. 50 c.c. of the wine are carefully boiled in a beaker for about 2–3 minutes, the vessel being removed from the flame and 2 c.c. of pure concentrated nitric acid added gradually and with stirring. This amount of acid is usually sufficient to turn even a deeply coloured wine a yellowish

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[1] As a rule 10 c.c. of the barium chloride solution suffice even for heavily plastered wines.

[2] If it is desired to use N/10-silver nitrate solution, 8·56 c.c. of this should be added per 50 c.c. of the wine.

colour ; if the latter does not appear, a few more drops of the acid are added, 10 c.c. of the silver solution are then added, the liquid being stirred, allowed to cool and filtered : if the filtrate gives a precipitate with the silver reagent, the wine is salted beyond the permissible limit.

2. Determination of the Chlorides.—50 c.c. of the wine, rendered faintly alkaline with caustic soda solution,[1] are evaporated to dryness in a platinum dish and the residue carefully incinerated as described on p. 190. The ash is extracted with hot water acidified with nitric acid and the chlorine determined in the solution obtained, which should be distinctly acid :

(a) *Volumetrically* by Volhard's method. A known volume of N/10-silver nitrate solution, more than sufficient to precipitate the chlorine present, is added and the excess measured, without filtration, by means of an equivalent ammonium thiocyanate solution, ferric alum being used as indicator : 1 c.c. N/10-silver nitrate = 0·003545 gram Cl = 0·00585 gram NaCl.

(b) *Gravimetrically.* The filtered nitric acid solution of the ash is precipitated with excess of silver nitrate in the usual way : AgCl ÷ 2·453 = NaCl.

16. Investigation of the Nitrates

The following methods may be employed :

1. WITH DIPHENYLAMINE. With a solution of diphenylamine in sulphuric acid, nitric acid gives a blue coloration.

Reagent. 0·1 gram of diphenylamine is dissolved in 100 c.c. of pure concentrated sulphuric acid.

Procedure. 100 c.c. of the wine are treated in a porcelain basin with a slight excess of slaked lime,[2] the liquid being evaporated to dryness and the residue, detached as far as possible from the walls of the vessel, well mixed with 30 c.c. of 95% alcohol. After 10 minutes the liquid is filtered into a small porcelain dish and evaporated on a water-bath. The residue is treated with 1 c.c. of distilled water and one-half of the liquid dropped carefully on to the sulphuric acid solution of diphenylamine in a wide testtube. If an intense blue coloration is obtained, the residual liquid is diluted with water and the test repeated ; in this way an idea of the amount of nitrate is obtained.

The reaction being very sensitive, it is necessary to make sure that none of the reagents employed contain nitric acid.

2. BY REDUCTION TO NITRITE. This is based on reduction of the nitrate to nitrite by ferrous sulphate and sulphuric acid and on the colour reaction of nitrous acid with starch paste and iodide.

Reagents. (a) A suspension of 1 gram of starch in 100 c.c. of water is heated on a water-bath and stirred until lumps disappear, 4 grams of pure zinc chloride being added and the heating on the boiling water-bath con-

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[1] The N/4-alkali used for determining the acidity of wine may be employed with advantage.

[2] Prepared by igniting carefully picked Carrara marble in a crucible and hydrating with distilled water.

tinued for half an hour. The liquid is then allowed to cool and 1 gram of potassium iodide dissolved in it.

(b) Saturated ferrous sulphate solution, which before use is boiled with iron wire and a few drops of pure sulphuric acid.

Procedure. 100 c.c. of the wine are evaporated in a flask to 10 c.c., allowed to cool and treated with 6 c.c. of the saturated ferrous sulphate solution and 4 c.c. of concentrated sulphuric acid.[1] The flask is connected with a vertical condenser about 50 cm. long and heated carefully over a small flame so that excessive frothing of the mass is avoided. The distillate is collected in two or three well-cleaned tubes, each containing 2–3 c.c. of the iodide-starch paste acidified with 2 drops of dilute sulphuric acid ; the tubes are inclined so that the distillate flows down the walls. In presence of nitrites, a blue ring forms at the zone of separation between the starch and the distillate.

This method may be associated with the preceding one in the case of sweet wines, which would froth considerably in presence of sulphuric acid. To this end the alcoholic liquid obtained as in 1 is diluted with a little water, the alcohol expelled and the liquid then distilled with ferrous sulphate and sulphuric acid, as just described.

17. Determination of the Total Phosphoric Acid

Phosphorus is present in wines as phosphates of calcium, potassium, magnesium, etc., and also in organic form, probably as acid glycerophosphate of potassium and calcium. The addition of phosphate, which sometimes replaces plastering, naturally increases the quantity of phosphorus present.

Phosphorus may be determined in either of the two following ways :

1. As MAGNESIUM PYROPHOSPHATE. The organic matter of the wine is oxidised by means of nitric acid and the phosphorus then estimated as magnesium pyrophosphate.

Reagents. (a) 150 grams of ammonium molybdate are dissolved in a litre of cold water and the solution poured into a litre of nitric acid of sp. gr. 1·2.

(b) Magnesia mixture, prepared by dissolving 68 grams of magnesium chloride and 165 grams of ammonium chloride in water, adding 260 c.c. of ammonia of sp. gr. 0·96 and making up to a litre with water.

Procedure. 200 c.c. of the wine are evaporated almost to a syrup in a porcelain dish over a naked flame, the residue being taken up in nitric acid (D 1·14) and the solution transferred to a half-litre flask so that the volume of the liquid with the acid used for rinsing out amounts to 150–200 c.c. The liquid is carefully evaporated to a small volume, 80–100 c.c. of the same acid being then added and the solution heated almost to dryness. If the liquid is brown, the addition of nitric acid is repeated ; it is then allowed to cool and 8–10 c.c. of concentrated sulphuric acid added, after which heat is applied. Immediately voluminous red vapours are developed and the liquid becomes dark ; on cooling, a few drops of concentrated nitric acid are introduced, the flask being slightly inclined.

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[1] The sulphuric acid should be free from nitrous products, the acid prepared by the contact process serving well.

If the liquid turns brown when heated, more nitric acid is added, this procedure being continued until the liquid remains white or only faintly yellow and is perfectly clear. On cooling, 50 c.c. of distilled water are added, then concentrated ammonia little by little until the reaction is almost neutral, and finally 100 c.c. of the molybdate solution; the whole is then heated on a water-bath and subsequently left in a warm place for 6 hours, after which the liquid is decanted on to a filter and the precipitate washed by decantation and dissolved in concentrated ammonia. The ammoniacal solution is filtered through the same filter into another beaker, the filter being washed with dilute ammonia. The ammoniacal solution is treated with hydrochloric acid until a permanent precipitate just begins to form and, after cooling, with 5 c.c. of ammonia; 10 c.c. of magnesia mixture are then added, gradually and with stirring, care being taken not to touch the sides of the beaker with the rod. Finally 40 c.c. of ammonia are added and the liquid left for a day and then filtered, the precipitate being washed with water containing ammonia (1 part of ammonia solution of sp. gr. 0·96 and 3 parts of water), dried and ignited. The weight of magnesium pyrophosphate from 200 c.c. of the wine, multiplied by 3·18775, gives the amount of phosphoric anhydride per litre.

2. As Ammonium Phosphomolybdate. The phosphoric acid is separated from the nitric acid solution of the ash as ammonium phosphomolybdate.

Reagent. 40 grams of powdered ammonium molybdate are dissolved in a mixture of 320 c.c. of water and 80 c.c. of 20% ammonia (D 0·925) and the solution poured into a cold mixture of 480 c.c. of 30% nitric acid (D 1·18) and 170 c.c. of water. The reagent should be left at rest for some days in the dark before use.

Procedure. 50 c.c. of the wine are evaporated in a platinum dish with about 1 gram of a mixture of nitre (1 part) and sodium carbonate (3 parts). The residue is charred, the carbonaceous matter washed with dilute nitric acid, the acid liquid filtered into a beaker, the residue washed with water and filter and residue thoroughly dried in an air-bath and incinerated in the original dish. The ash is moistened with nitric acid and taken up in boiling water, the solution being filtered into the beaker in which the first acid filtrate was collected and the filter and dish washed several times with hot water.

The acid liquid is evaporated to about 10 c.c. and, when its temperature has fallen to 50°, treated with 50 c.c. of the ammonium molybdate reagent at 45–50°.

After some time, 7–8 grams of ammonium nitrate are added and the liquid stirred to dissolve the salt and heated for about an hour at 45–50° C.

The ammonium phosphomolybdate thus obtained is collected in a tared Gooch crucible charged with asbestos and washed with water acidified with 1% of nitric acid (D 1·18) until a drop of the filtrate leaves no residue when evaporated on a watch-glass; the crucible is heated in an oven at 70–80° to constant weight: ammonium phosphomolybdate × 0·0378 = phosphoric anhydride.

18. Detection of Citric Acid

Dénigès' reaction is used, the procedure being as follows :

Reagents. (*a*) Mercury sulphate solution obtained by dissolving 5 grams of mercuric oxide in 100 c.c. of water and 20 c.c. of concentrated sulphuric acid.

(*b*) 2% potassium permanganate solution.

Procedure. 10 c.c. of the wine are shaken with about 1 gram of lead peroxide, 2 c.c. of the mercuric sulphate solution being then added and the solution again shaken and filtered. To 5–6 c.c. of the filtrate, heated to boiling, are added a drop of the permanganate solution and, after decolorisation, 9 other drops in the same manner. Normal wines give only a slight turbidity, whilst those acidified with citric acid show an intense turbidity or, when the amount of the acid exceeds about 0·5 gram per litre, a white, flocculent precipitate. It is well to make control tests with natural wines and with others containing known amounts of citric acid.

19. Detection of Free Mineral Acids

The acid most commonly added to wines is sulphuric acid. The method of testing is based on the difference in the way the electrical conductivity varies in a natural wine and in a wine containing mineral acid when small quantities of caustic alkali are added. With a natural wine the conductivity is increased by such addition, whilst one containing mineral acid shows first a diminution of conductivity, which increases only when all the free acid is neutralised. The following apparatus and reagents are required [1] :

Apparatus. (I) A Wheatstone bridge (Kohlrausch modification) represented diagrammatically in Fig. 53 and including :

(*a*) A small induction coil I furnished with an interruptor which can vibrate very rapidly and so produce a buzzing sound.
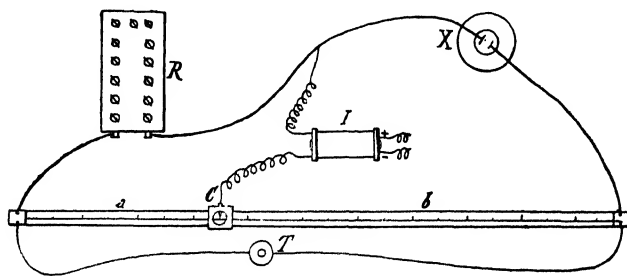
FIG. 53

(*b*) A platinum wire about 0·2 mm. in diameter, uniformly calibrated and stretched along a scale 1 metre long, divided into millimetres and fitted with a movable index C, which serves to make contact with the wire.

(*c*) A resistance box R, exactly calibrated.

(*d*) A small telephone receiver T.

[1] G. Bosco and R. Belasio : *Annali di Chim. applic.*, Vol. V, p. 233.

(2) A cell X, formed of a glass cylinder 3·5 cm. in diameter, closed with an ebonite lid traversed by a thermometer reading to tenths of a degree and by two glass tubes which are filled with mercury and to the ends of which are fused two electrodes of platinised platinum $E\,E$,[1] these being arranged either horizontally (Fig. 54) or vertically (Fig. 55) and about 1 cm. apart.

(3) A thermostat consisting of a water-bath to maintain the liquid in the cell at a constant temperature, since the different readings must be made at the same temperature.

Reagent. N/10-potassium hydroxide solution.

Arrangement of the apparatus. This is shown diagrammatically in Fig. 53. The alternating current from the induction coil I flows to the contact C and to the wire joining the rheostat R with one of the plates of the cell X, there dividing into two currents, one flowing through the known resistance R and the part a of the wire and the other, by means of two copper wires
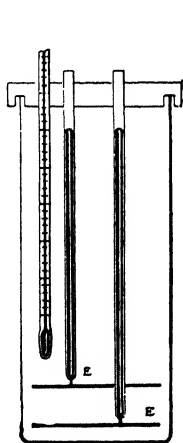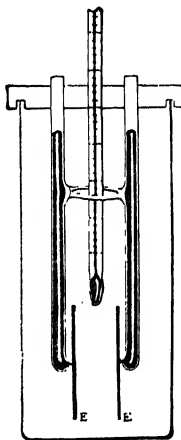
FIG. 54   FIG. 55

dipping into the mercury tubes, through the cell X and then through the part b of the stretched wire. To the two ends of the latter the telephone receiver T is connected. Fig. 56 gives a general view of the apparatus.

Procedure. Some of the wine is vigorously shaken to expel most of the carbon dioxide present and, after standing, exactly 20 c.c. are made up with water to 100 c.c. in a measuring flask. Of this diluted wine, 25 c.c. are introduced into the cell, care being taken that no gas-bubbles remain adherent to the electrodes. The cell is then placed in the thermostat and introduced into the circuit. When the temperature of the electrolyte has become constant, the induction coil is started and the resistance of the rheostat regulated (with the cell described, about 150 ohms will be

[1] The electrodes are platinised by immersion in a 3% platinum chloride solution containing 0·02–0·03% of lead acetate and passage of a continuous current of 0·2–0·3 amperes, the poles of the current being frequently inverted. Electrodes thus platinised should be velvety-black.

required) so that the telephone receiver gives the minimal sound when the movable index is at about the middle of the scale ; the exact point on the scale is read off.

The plates are then removed from the cell and the latter, carefully taken from the thermostat : 0·1 c.c. of N/10-caustic potash solution is then added from a graduated pipette, the end of which touches the wall of the cell as near as possible to the surface of the liquid. The latter is mixed—care being taken that no bubbles remain adhering to the electrodes—and the cell again placed in the thermostat and a second reading taken at the same temperature as the first. Successive readings are made in the same way after addition of successive tenths of a c.c. of the N/10-alkali.

In this way are obtained a number of values of a (mm.), i.e., the distances from the zero of the scale to the position of the movable contact giving the minimal sound in the telephone receiver.
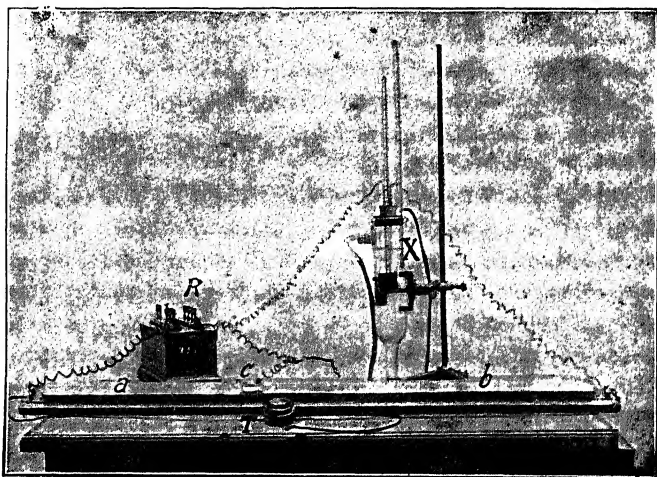
Fig. 56

To follow the variation of the conductivity as alkali is added, the values of $a : b$ are calculated, b having the value ($1000 - a$). The values of this ratio are given in Table XXIII.

If $a : b$ increases continuously, the wine contains no free acid, but if it first diminishes and only increases after a certain amount of alkali has been added, the presence of free mineral acid may be concluded. It is convenient to represent graphically the relation between the values of $a : b$ and of the amounts of alkali added.

EXAMPLES : (1) 25 c.c. of a red wine, diluted 1 to 5, gave an initial value of a, 490 mm. ; after successive additions of 0·1 c.c. of N/10-KOH, the values of a were 495, 500, 505, 510, 516, 521 and 527 mm. Thus $a : b$ continually increases and the wine does *not* contain free mineral acid.

(2) Similarly, another red wine, diluted 1 : 5, gave readings of 556, 554, 553, 552, 551, 552, 554, 556 and 559 mm. As these first fall and then rise,

TABLE XXIII

Values of a : b

cm.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
40	0·668	0·668	0·672	0·675	0·677	0·680	0·683	0·686	0·689	0·692
41	0·694	0·697	0·700	0·703	0·706	0·709	0·712	0·715	0·718	0·721
42	0·724	0·727	0·730	0·733	0·736	0·739	0·742	0·745	0·748	0·751
43	0·754	0·757	0·760	0·763	0·766	0·769	0·773	0·776	0·779	0·782
44	0·785	0·788	0·792	0·795	0·798	0·801	0·805	0·808	0·811	0·814
45	0·818	0·821	0·824	0·828	0·831	0·834	0·838	0·841	0·845	0·848
46	0·851	0·855	0·858	0·862	0·865	0·869	0·872	0·876	0·879	0·883
47	0·886	0·890	0·893	0·897	0·901	0·904	0·908	0·912	0·915	0·919
48	0·923	0·926	0·930	0·934	0·938	0·941	0·945	0·949	0·953	0·957
49	0·960	0·964	0·968	0·972	0·976	0·980	0·984	0·988	0·992	0·996
50	1·000	1·004	1·008	1·012	1·016	1·020	1·024	1·028	1·033	1·037
51	1·041	1·045	1·049	1·053	1·058	1·062	1·066	1·070	1·075	1·079
52	1·083	1·088	1·092	1·096	1·101	1·105	1·110	1·114	1·119	1·123
53	1·128	1·132	1·137	1·141	1·146	1·151	1·155	1·160	1·165	1·169
54	1·174	1·179	1·184	1·188	1·193	1·198	1·203	1·208	1·212	1·217
55	1·222	1·227	1·232	1·237	1·242	1·247	1·252	1·257	1·262	1·268
56	1·273	1·278	1·283	1·288	1·293	1·299	1·304	1·309	1·315	1·320
57	1·326	1·331	1·336	1·342	1·347	1·353	1·358	1·364	1·370	1·375
58	1·381	1·387	1·392	1·398	1·403	1·410	1·415	1·421	1·427	1·433
59	1·439	1·445	1·451	1·457	1·464	1·470	1·475	1·481	1·488	1·494
60	1·500	1·506	1·513	1·519	1·525	1·532	1·538	1·545	1·551	1·558

presence of free mineral acid is indicated. Indeed, 0·075‰ of sulphuric acid had been added to this wine

When the apparatus is fitted up, the test is rapid and also fairly sensitive, any quantity of sulphuric acid exceeding 0·05‰ being detectable

20. Detection and Determination of Antiseptics

The antiseptics most commonly used for the preservation of wine are sulphur dioxide, salicylic acid, boric acid, fluorides, abrastol, formaldehyde and urotropine. They are detected and determined as follows:

1. Sulphur Dioxide. This is determined by converting it into sulphuric acid by means of aqueous iodine solution and estimating either the amount of iodine used up in the oxidation or the sulphuric acid formed. It should be borne in mind that sulphur dioxide oxidises with great ease in contact with the air, so that it should be determined as soon as the bottle is opened and without filtering the wine.

(*a*) TOTAL SULPHUR DIOXIDE.

Reagents. (1) N/20-iodine solution containing 6·33 grams of iodine per litre, 9·5 grams of potassium iodide per litre being added to dissolve the iodine.

(2) Sodium thiosulphate solution containing 12·40 grams of the crystallised salt ($Na_2S_2O_3 + 5H_2O$) per litre.

(3) Starch paste (*see* Vol. I, p. 379).

To determine the titre of the sodium thiosulphate with respect to the

iodine, 20 c.c. of a solution containing 3·874 grams of pure potassium dichromate per litre are shaken with 10 c.c. of 10% potassium iodide solution and 5 c.c. of hydrochloric acid (D 1·1) and then diluted with about 100 c.c. of water, the iodine liberated being titrated with the thiosulphate solution in presence of starch paste ; the 20 c.c. of dichromate solution set free exactly 0·2 gram of iodine.

Procedure. A stout-necked, round-bottomed flask of about 300 c.c. capacity is closed by a rubber stopper through which pass (1) a tapped funnel, (2) a glass tube drawn out to a point and reaching almost to the bottom of the flask and (3) a glass tube connected with a vertical spiral condenser. The end of the condenser is tightly connected with either a bulbed tube of about 75 c.c. capacity or other absorption apparatus.

The air is completely expelled from the apparatus by means of a current of carbon dioxide passed through the drawn-out tube and 50 c.c. of the standard iodine solution introduced into the absorption tube. Through the tapped funnel 100 c.c. of the wine and 2 c.c. of concentrated hydrochloric acid are poured into the flask, which is then carefully heated until half the wine has distilled over, the current of carbon dioxide being maintained meanwhile. The iodine solution, which should still be brown, and the rinsings of the absorption tube are titrated in a beaker with the thiosulphate solution in presence of starch paste. The number of c.c. of iodine solution reduced, multiplied by 0·016, gives the total sulphurous acid per litre of the wine.

If loss of iodine is feared owing to an excessive current of carbon dioxide, the liquid from the absorption tube is boiled for a quarter of an hour under a reflux condenser and the sulphuric acid then precipitated and determined as barium sulphate : $BaSO_4 \times 2·744 = SO_2$ per litre of the wine.

(*b*) COMBINED SULPHUR DIOXIDE.[1] This is determined by means of iodine solution after the free sulphur dioxide has been transformed directly in the wine into sulphuric acid.

Reagents. (1) Solution containing 2·5 grams of iodine and 3·5 grams of potassium iodide per litre.

(2) Sodium arsenite solution prepared by heating 1 gram of arsenious acid and 3 grams of pure sodium carbonate with 600–700 c.c. of water and making up the cold liquid to a litre. Solutions (1) and (2) should exactly correspond.

(3) N/20-iodine solution, N/20-sodium thiosulphate solution, and starch paste prepared as in (*a*).

Procedure. The volume of iodine solution (1) required to oxidise the free sulphurous acid in 10 c.c. of the wine is first approximately determined, starch paste being used as indicator; if the wine is red and highly coloured, it should be suitably diluted. In a flask arranged as for the preceding determination (*a*), 100 c.c. of the wine, 2 c.c. of concentrated hydrochloric acid and the necessary amount of the iodine solution are placed. After some minutes sodium arsenite solution is added in amount corresponding with the iodine solution used and hence capable of destroying the whole of the iodine added.

[1] Mathieu and Billon, *see* U. Gayon and J. Laborde : *Vins* (Paris and Liège, 1912), p. 148.

The combined sulphurous acid, which has not been attacked by the iodine is next determined as in (*a*), either by titrating the residual iodine in the absorption tube or by estimating the sulphuric acid formed.

(*c*) FREE SULPHUROUS ACID. This is represented by the difference between the total and combined sulphurous acid. It may be checked by determining the sulphates in the residues after the total and combined sulphurous acids have been distilled; the difference between these two gives the sulphate corresponding with the free sulphurous acid: $BaSO_4 \times 2.744 = SO_2$ per litre.

2. Salicylic Acid.—Use is made of the violet coloration with ferric chloride, the procedure being as follows:

50 c.c. of the wine, acidified with a few drops of dilute hydrochloric acid, and 50 c.c. of a mixture of ether and petroleum ether (equal volumes) are mixed in a separating funnel by inverting the latter repeatedly, care being taken not to emulsify the liquid. When the ethereal liquid has completely separated, it is filtered through a dry filter and left to evaporate spontaneously. The dry residue is dissolved in a few c.c. of water and the solution treated drop by drop with a neutral ferric chloride solution so dilute as to be scarcely coloured (dilute ferric alum solution may also be used). A distinct violet coloration indicates the presence of salicylic acid.

If the addition of the ferric salt produces a brownish coloration owing to the presence of tannin in the solution and so masks any coloration due to salicylic acid, it is necessary to repeat the extraction on the residue obtained, after acidifying it with a few drops of dilute hydrochloric acid.

Carbon disulphide may also be used as solvent.

Some natural wines contain substances which may give a feeble violet coloration, so that only when a distinct positive reaction is obtained with the above procedure can the presence of salicylic acid be affirmed.

3. Boric Acid.—Use is made of the orange-red coloration given by turmeric in presence of a solution of a borate acidified with hydrochloric acid.

(*a*) DETECTION. 50 c.c. of the wine are evaporated in a platinum dish and incinerated in presence of sodium carbonate, the ash being taken up in 5 c.c. of hydrochloric acid diluted to 10%. Into the solution is dipped a strip of curcumin paper,[1] which is dried on a clock-glass over a water-bath. If the paper assumes an orange-red coloration, changed to blackish-blue by a drop of a 2% solution of anhydrous sodium carbonate, boric acid is present.

This test is sensitive only in presence of at least a milligram of boric acid in the hydrochloric acid solution. Consequently, a positive result indicates certain addition of boric acid to the wine, since the test is not sufficiently sensitive to detect the traces of boric acid (up to 0.002 gram per litre) which may be found in certain natural wines from volcanic regions.

(*b*) QUANTITATIVE DETERMINATION. The coloration given by the hydrochloric acid solution of the ash in presence of turmeric is compared with those obtained with solutions containing known quantities of boric acid.

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[1] For the preparation of this paper *see* this volume, p. 8.

100 c.c. of the wine, rendered faintly alkaline by means of a 10% solution of pure sodium carbonate solution, are evaporated on a water-bath and the residue calcined until the ash is quite free from carbon. The ash is treated with 5 c.c. of hydrochloric acid diluted to 10% and the solution poured into a test-tube, while the dish is washed with 15 c.c. of 95% alcohol and this also introduced into the test-tube, 15 c.c. of hydrochloric acid (D 1·19) being then added. After cooling, the liquid is treated with 0·2 c.c. of a 0·1% alcoholic solution of pure curcumin,[1] mixed and left in the dark for half an hour. In presence of a larger or smaller proportion of boric acid, the liquid assumes a coloration varying from an intense red to a pale pink, whilst in absence of boric acid it remains yellow.

If the test gives a positive result, a 1% boric acid solution is prepared and with varying quantities of this a series of tests are made with the same amounts of acid, alcohol and curcumin as are used in the case of the wine. By comparison of the colours, the amount of boric acid in the wine may be judged.

When the ash, on treatment with hydrochloric acid, is seen to contain a considerable proportion of iron, the latter should be eliminated in order that exact results may be obtained. The ash, acidified with hydrochloric acid, is rendered alkaline with sodium hydroxide solution to precipitate the iron, the mixture being heated and filtered and the residue washed with boiling water until the filtrate is no longer alkaline ; the filtrate is evaporated to dryness and the dry residue tested as described above.

4. Fluorides.—Fluorides are detected by liberating the hydrofluoric acid and characterising the latter by its corrosive action on glass, the method of Blarez and Vandam [2] being used :

100 c.c. of the wine are mixed in the cold with a few drops of 20% sodium sulphate solution and 10 c.c. of 10% barium acetate solution and left to settle for 12 hours, by which time a clear liquid usually separates over a voluminous precipitate ; the greater part of the clear liquid is then decanted off. If, however, the decanted liquid is still turbid, it is boiled and filtered hot. In either case the precipitate remaining on the bottom of the vessel is collected on the filter previously used, washed with a little distilled water, dried in an oven at 100–110° and incinerated with the filter in a platinum crucible.

The ash is then treated with 1 or 2 drops of water and a few drops of concentrated sulphuric acid. A rubber ring is at once fixed round the edge of the crucible and on this is placed a thin sheet of glass coated on the lower side with carnauba wax or high melting point paraffin wax, portions of which have been scratched off with a wooden point. The rubber ring ensures perfect contact with the glass strip and prevents loss of the hydrofluoric acid vapour. The crucible is then placed on an asbestos card, which is gently heated with a small flame for about half an hour. Fusion of the wax is prevented by placing filter-paper soaked in water on the glass and a small thin-walled beaker of ice and water on the filter-paper.

[1] *See* footnote, p. 8.
[2] *Ann. de chim. analyt.*, 1905, p. 73 ; 1907, p. 466 ; *Ann. des Falsifications*, 1909, 2, p. 160.

When the heating is over, the glass is removed, heated and cleaned with a cloth soaked in petroleum ether. If the wine contains fluoride, the glass will show persistent etching, visible to the naked eye. No attention is paid to images which appear when the glass is breathed on but disappear when the glass dries.

5. Abrastol (calcium β-naphtholsulphonate).—This is decomposed by prolonged boiling with hydrochloric acid into calcium sulphate, sulphuric acid and β-naphthol, the last being then identified.

200 c.c. of the wine are boiled for an hour in a reflux apparatus, or heated for 3 hours on a water-bath, with 8 c.c. of hydrochloric acid. When cold, the liquid is shaken with 50 c.c. of petroleum ether and the ethereal layer filtered and evaporated on a water-bath at as low a temperature as possible. The residue is dissolved in 10 c.c. of chloroform and the solution boiled for 2 minutes in a test-tube with a piece of caustic potash and a few drops of alcohol. Any abrastol present is thus converted into β-naphthol which, with the potash, gives a deep blue coloration rapidly changing to brown and then to yellow.

If the wine contains only a small quantity of abrastol, the chloroform turns greenish and the lump of potash blue.

6. Formaldehyde.—This is tested for in the first portions of the distillate of 100 c.c. of the wine by means of the reactions characteristic of formaldehyde (*see* Beer, p. 170).

Wines may contain formaldehyde derived from urotropine (hexamethylenetetramine) used to desulphite them. In this case 50 c.c. of the wine are acidified with 10 drops of sulphuric acid and distilled slowly. The first 10 c.c. of distillate are discarded and the next 20 c.c. divided into two portions and tested for formaldehyde.

21. Artificial Sweetening Agents

These are usually saccharin (and the saccharinates) and dulcin or sucrol.

1. Saccharin.—This is detected and determined as follows :

In a porcelain dish 250 c.c. of the wine are evaporated on the water-bath to about one-half the volume to expel the alcohol, and the residue and the water used for rinsing out the dish returned to the measuring flask. The hot liquid is acidified with 3 c.c. of concentrated acetic acid and then cooled and treated with 20 c.c. of a 20% solution of normal lead acetate.[1]

After about half an hour, the excess of lead is eliminated by addition of 40 c.c. of a solution containing 10% of sodium phosphate and 10% of sodium sulphate, and the volume made up to 250 c.c. by means of distilled water. The liquid is mixed, left until the precipitate settles and filtered through a dry filter, exactly 200 c.c. of filtrate being collected.

This liquid is evaporated on a water-bath to about 60–70 c.c. and transferred to a separating funnel, where it is acidified with 10 c.c. of dilute phosphoric acid (1 : 3) and shaken vigorously with about 100 c.c. of a mixture in equal volumes of ether and benzene. When the two layers have separated well, the lower aqueous liquid is run off into a flask. By

[1] A. Bianchi e E. Di Nola : *Boll. chim. farmaceutico*, XL VII, p. 559.

gentle rotation and shaking of the funnel, the aqueous acid drops adhering to the walls are caused to collect at the bottom and are then added to the acid liquid in the flask. The ether-benzene mixture is then poured into another separating funnel, and the extraction of the aqueous liquid repeated once or twice in the same way. The united ethereal liquids are washed by energetic shaking with a few c.c. of water and, after removal of the latter, are filtered through a double dry filter into a beaker.

The bulk of the filtrate is distilled off and the remaining liquid evaporated to dryness in a porcelain dish on a water-bath, together with a few c.c. of the distillate with which the distilling flask is rinsed. The residue is dissolved in the hot in about 50 c.c. of distilled water and while the dish is kept on a water-bath and the liquid stirred with a rod, an approximately normal solution of permanganate is added drop by drop. The addition of permanganate, which is for the purpose of destroying any substances extracted along with the saccharin, is discontinued when the liquid remains pink for some minutes.

The liquid thus obtained is filtered into a separating funnel, acidified with dilute phosphoric acid and shaken vigorously with an equal volume of ether. The procedure described above is followed, the extraction being repeated two or three times and the united ethereal liquids washed by shaking with 3–4 c.c. of water. After removal of the water most of the ether is distilled off and the remainder of the liquid and a few c.c. of the distillate used to rinse out the flask transferred to a tared glass dish and evaporated to dryness at a gentle heat, and the residue weighed.

If this residue does not taste sweet, the wine does not contain saccharin, but if it has a persistent sweet taste, the presence of an artificial sweetening agent is certain. Saccharin is identified as follows :

(a) *By the melting point.* If there is sufficient of the residue, its m.pt. is determined (m.pt. of saccharin, 224°)—after recrystallisation if it is not perfectly colourless and crystalline.

(b) *By conversion into salicylic acid.* For this purpose a little of the sweet residue is dissolved in a few c.c. of alcohol and to the solution in a test-tube is added a small piece of caustic soda. The liquid is then heated in a paraffin wax bath, slowly at first to expel the alcohol and afterwards rapidly to about 260°, this temperature being maintained for some minutes. When cold the residue is dissolved in a little water and the solution placed in a small separating funnel, acidified slightly but distinctly with dilute sulphuric acid and the salicylic acid formed extracted by shaking the liquid with an equal volume of ether. The ethereal solution is carefully evaporated and the residue treated with a fresh, very dilute solution of ferric chloride. If the wine contains saccharin, the characteristic violet coloration will be given by the salicylic acid formed by the action of the alkali on the saccharin.

(c) *By testing for sulphur.* The sulphur contained in the saccharin (orthobenzoicsulphinide) is converted into sulphuric acid by fusion with pure potassium nitrate and sodium carbonate in the following manner :

The remainder of the sweet residue is treated with a few c.c. of a dilute sodium carbonate solution and the liquid filtered into a platinum dish and

.evaporated to dryness. The residue is mixed with 4–5 times its weight of powdered sodium carbonate and the mixture gradually added to fused nitre.

When cold, the product of the reaction is taken up in water and the solution acidified with hydrochloric acid and treated with barium chloride for the detection of sulphuric acid.

The method given above is, of course, applicable to the detection of either saccharin or its compounds, of which the most commonly used are the sodium, ammonium and magnesium derivatives.

2. Dulcin.—When the residue from the extraction with the ether-benzene mixture is sweet, whilst the presence of saccharin is excluded by the reactions indicated above, tests are made for other artificial sweetening materials, among them dulcin.

For this purpose, another portion of the wine (250–500 c.c.) is treated by the method used for the extraction of saccharin. In the residue from the evaporation of the ether-benzene mixture, dulcin is identified as follows :

(*a*) Part of the residue is heated carefully for a short time with 2 drops of phenol and 2 of concentrated sulphuric acid. The reddish-brown syrup is diluted with a few c.c. of water, and on to the solution in a test-tube are poured a few drops of ammonia or sodium hydroxide solution. If the residue contains dulcin, the zone of contact between the two liquids exhibits a blue or violet-blue coloration according as ammonia or soda is used.

(*b*) Another part of the residue is suspended in 5 c.c. of water, treated with 2–4 drops of mercuric nitrate solution [1] and boiled for 5–10 minutes. In presence of dulcin the liquid becomes violet, the distinctness of the coloration being enhanced by addition of lead peroxide.

22. Detection and Determination of Extraneous Metals

Wine may contain metals either due to practices which are not permissible (aluminium—owing to the presence of alum—barium, strontium) or derived from the vessels in which the wine has been kept or from mixtures used to combat diseases of the vines (copper, lead, zinc).

They are detected by analysis of the ash, especially in the following manner :

1. Alum.—Alum is usually added to wines to restore the colour, to clarify them, to impart a more astringent taste and often to mask watering. It is determined by precipitating the aluminium as hydroxide and weighing as oxide.[2]

500 c.c. of the wine are evaporated to dryness and the residue charred, the carbonaceous mass being powdered and boiled with dilute hydrochloric acid for a few minutes. The liquid is filtered into a platinum or porcelain

[1] From 1 to 2 grams of freshly precipitated yellow mercuric oxide are dissolved in nitric acid and the liquid treated with caustic soda solution until a small quantity of precipitate is formed, diluted with water to 15 c.c. and decanted.

[2] In examining a wine in which alum is suspected, it is important to analyse any sediment, since a large part of the alum is gradually deposited in this in the form of insoluble aluminium phosphate.

dish, the residue washed with hot water acidified with hydrochloric acid, and the filtrate heated to boiling and treated with excess of pure sodium hydroxide.

In this way, the iron hydroxide and the phosphates of the alkaline earths remain undissolved, whilst the alumina passes into solution. After standing for some time on a water-bath, the liquid is filtered into a platinum or porcelain dish and the residue washed with hot water. The filtrate is boiled for 2–3 minutes with excess of ammonium chloride, the aluminium being thus precipitated as hydroxide, which is collected in a filter supported by means of a small platinum cone in the funnel and washed with hot water containing a little ammonium chloride and ammonia, slight suction being applied at the end of the washing.

The precipitate is dissolved in a little hot dilute hydrochloric acid and the aluminium hydroxide reprecipitated with ammonium chloride and ammonia. The precipitate is allowed to settle, washed by decantation and then on the filter with slightly ammoniacal hot water. The weight of oxide obtained after igniting in a platinum crucible in a blowpipe flame is multiplied by two and the result diminished by the quantity normally present in wine (0·01–0·04 gram Al_2O_3 per litre). The remainder is calculated as alum.

2. Lead, Copper, Zinc.—500 or 1000 c.c. are evaporated to small volume, treated with excess of hydrochloric acid and then, while heated on a water-bath, wtih small quantities of potassium chlorate until the liquid is as nearly colourless as possible. This liquid, which contains any of the above metals present, is diluted with water, heated, and subjected to the action of a current of hydrogen sulphide. Any precipitate, which will contain lead and copper sulphides, is collected on a small filter, while the filtrate is tested for zinc according to (c). The precipitate, washed with hydrogen sulphide solution and dried, is ignited with the filter in a porcelain dish. The residue is taken up in a little nitric acid (D 1·2), gently heated, diluted with a little water and filtered into a porcelain dish, the filtrate being used for the detection of lead as in (a) and for that of copper, as in (b).

(a) *Detection of lead.* The filtrate is evaporated with 1–2 c.c. of dilute sulphuric acid until white fumes develop, a precipitate of lead sulphate being formed if lead is present. Confirmation is obtained by collecting the precipitate, dissolving it in a few c.c. of a hot, concentrated ammonium tartrate solution and testing with potassium chromate.

(b) *Detection of copper.* The filtrate from the lead sulphate is made alkaline with ammonia, a more or less intense blue coloration being obtained in presence of copper. As a confirmatory test, part of this liquid is acidified with acetic acid and the copper precipitated with a drop of potassium ferrocyanide solution.

(c) *Detection of zinc.* The filtrate from the lead and copper sulphides is boiled to eliminate the hydrogen sulphide and 1 or 2 drops of nitric acid added to oxidise the traces of iron present. The liquid is then rendered alkaline with ammonia to separate the phosphates and filtered, the filtrate being acidified with acetic acid and part of it treated with hydrogen sulphide,

which will give a white precipitate in presence of zinc, while another part is tested with a drop of potassium ferrocyanide.

3. Barium and Strontium.—The ash from 100 c.c. of wine, prepared in the usual way, is taken up in dilute hydrochloric acid and the filtered solution evaporated to dryness, the residue being examined spectroscopically for barium and strontium. If these are present, they are determined by the ordinary methods.

23. Microscopic Examination

Examination is made of a drop of the deposit obtained when the wine is either allowed to stand or centrifuged or, with very turbid wine, a drop of the latter itself may be examined. A magnification of 500 diameters is first used, but detection of the smallest bacteria requires about 1000 diameters.

The organisms may be fixed and stained as follows : A drop of the wine or deposit is evaporated on a microscope slide placed on an asbestos sheet heated at 60°, the dry residue being passed rapidly through a bunsen flame so as not to cause browning. The slide is cooled and immersed for 5 minutes in aqueous fuchsine solution or, better, in gentian violet prepared by mixing 10 c.c. of a saturated solution of the violet in 95% alcohol with 100 c.c. of water and adding 1 gram of phenol. The preparation is carefully washed with water, which removes the excess of the stain but leaves the coloured micro-organisms adhering to the slide.

Of the different organisms causing alterations and diseases in wine, only those associated with " fleurs de vin " and acetous fermentation can be identified with certainty.

Fleurs de vin is due to Mycoderma vini, which is elliptical in form and exhibits two or three distinct vacuoles.

Acetous fermentation (*souring*) is caused by Mycoderma aceti, which consists of oval cells with a marked constriction in the middle, resemblance to the figure 8 being thus produced. The cells are considerably smaller (about 10 times) than those of M. vini. In some cases several individuals are joined in a chain.

As regards other organisms which are the cause of serious alterations in wines, uncertainty still exists as to their identity. The most recent investigations indicate that they are capable of different functions and thus yield different products, one or another disease being caused according to the conditions under which they exist.

Tourné or *poussé* wines exhibit principally rod- or thread-like micro-organisms, which appear rigid and are sometimes joined at the ends and sometimes angular ; *bitter* wines show thin, stiff bacilli, 5–6μ long, sometimes united and encrusted with the colouring matter of the wine.

<p align="center">*
* *</p>

The most important *conclusions* to be drawn from the analysis of a wine are those giving indications as to its *genuineness,* and the certainty and ease with which they attain this end vary in the three following cases.

(*a*) *A sample of the genuine wine is available for comparison.* In this case

it is sufficient to determine in the two wines those components which are of special interest in relation to the scope of the analysis. If any differences occur, the way in which the wine has been treated will be evident. Thus, if a wine exhibits general and proportional deficiencies of its constituents, mere watering is proved, and the extent of this may be calculated. If, however, as frequently happens, besides watering, addition of tartaric acid has occurred, the alcoholic strength will be lowered, but the acidity will not be lowered in the same proportion, and so on.

(b) *No genuine sample is available, but information as to the origin and quality of the wine.* In this case the analytical data obtained are considered, both as regards any regular relations between the various components and in comparison with those of genuine wines of the same type from the same or a neighbouring district and if possible of the same season. The analyst should, therefore, have at his disposal as complete as possible a list of analyses of genuine wines from different regions, with data referring at least to the principal constituents, viz., the alcohol, acidity, extract, ash and sugars.

(c) *Nothing is known as to the origin of the wine.* In this case judgment presents the greatest difficulty, being necessarily based on the analytical data. The latter must be considered to ascertain if they are normal with respect to those usually accepted and if the relations between them correspond with what have been established for genuine wines.

In every case the general criteria and data to be borne in mind in the evaluation of the data obtained on analysis of a wine are as follows:

Physical characters. After standing, a sound, genuine wine should be perfectly clear and of a clean, brilliant colour; it should have a characteristic vinous odour, unmixed with other odours denoting disease or defects in the wine.

Alcohol. The proportion of alcohol varies from a minimum of 6–7% by volume to 16–17%.

Addition of alcohol (fortification) may be proved either by comparison with the alcohol content of genuine wines of the same origin and type or, if such data are lacking, by means of the glycerine-alcohol ratio. A less proportion of glycerine than 7 per 100 of alcohol may be taken as an indication of fortification.

Extract. This varies from about 15 to about 45 grams per litre. The lowest values are found especially with white wines, while red wines, especially " vins de coupage," have usually somewhat higher extracts. The extract is sometimes increased by addition to the wine of dextrin and glycerine.

Ash. In ordinary wines the weights of ash and extract are approximately in the ratio 1 : 10. A greater proportion of ash may be due to some treatment of the wine, such as plastering, addition of alkaline salts to correct acidity, salt, phosphate, alum, or impure mineral substances (kaolin, Spanish clay) used as clarifying agents.

Total alkalinity of the ash. This alkalinity, expressed in c.c. of N-alkali per litre is, on the average, ten times the number of grams of ash per litre. A low value of the alkalinity of the ash may indicate some treatment of the wine such as plastering or addition of phosphate of free mineral acid, resulting in decomposition or precipitation especially of the potassium bitartrate, on which the alkalinity of the ash largely depends.

Total acidity. This acidity, expressed as tartaric acid, varies from 4–5 to 15–16 grams per litre. Wines rich in alcohol are relatively less acid than those of low alcohol content, owing to precipitation of the potassium bitartrate by the alcohol. Further, the total acidity of a wine diminishes as the wine ages, in consequence of precipitation of this salt and also of the tannin and likewise of decomposition of the malic acid into lactic acid of one-half the equivalent acidity. On the other hand, the total acidity may be increased indirectly as a result of certain diseases of the wine which increase the volatile acidity.

When necessary, the acidity of a wine is augmented by addition of tartaric or citric acid, and mineral acids, especially sulphuric acid, are sometimes used.

Volatile acidity. In ordinary red wines this acidity is, on the average, 0·4–0·8 gram per litre, expressed as acetic acid, and in white wines is somewhat less. In some wines, rich in alcohol and extract, such as " vins de coupage," it may surpass the above limits without producing an acetous character. In any case, however, if the volatile acidity exceeds 2 grams per litre, the wine is unsuitable for consumption.

Sugars. These vary in amount with the quality and type of the wine. Sweet wines may contain marked quantities—even more than 15%—especially if derived from must from withered grapes. In ordinary dry wines, the sugars vary from 5 to 20 grams per litre, a small portion being pentoses and consequently unfermentable. Wines do not naturally contain saccharose, which is, however, sometimes added, more particularly to must poor in sugars.

Glycerine. This is a normal product of the alcoholic fermentation of grape must, 7–14 grams per 100 grams of alcohol being regarded as the limiting amounts thus produced.

Glycerine may be added to wine either to mask fortification by restoring the alcohol-glycerine ratio to its normal value or to disguise watering by increasing the proportion of extractive matters. Glycerine is also added to wine which is too harsh or astringent. When of considerable extent, such addition is detected by means of the glycerine-alcohol ratio, which should not exceed 14 : 100.

Colouring matters. The *colour* of wine is due to a group of colouring matters known as œnocyanins and it constitutes, especially as regards its tone and brilliancy, one of the most valued qualities of wines, particularly of those to be used for correcting poorer wines. In this case special importance attaches to the froth, which should be a brilliant garnet-red. As a result of the action of atmospheric oxygen or of special processes of decomposition, the colouring matter of wine undergoes transformation into insoluble products, so that, with age, wine tends to become decolorised.

In close relation to the colouring matters are the tannins, the amount of which may be as high as 4–5 grams per litre. Tannin also tends to disappear with lapse of time, partly by precipitation and partly by decomposition. Tannin is sometimes added to wine, on which it exerts a preservative action, mainly in virtue of its property of coagulating albumin.

Sulphates. The amount of sulphate in wine, expressed as potassium sulphate, varies from 0·2 to 0·6 gram per litre. This quantity may, however, be considerably increased as a result of *plastering* or addition of calcium sulphate during the fermentation of the must.

This treatment is permitted [in Italy] provided that the wine, when ready for consumption, contains not more than 2 grams of sulphate, calculated as potassium sulphate, per litre ; with choice wines containing not less than 15% of alcohol by volume, greater plastering is allowed.

Plastered wines show increased ash, while the alkalinity of the latter is diminished. These wines are sometimes subjected to de-plastering, that is elimination of part of the sulphate, by barium or strontium salts, but this treatment is not permissible and these elements should not be found in genuine wines.

Phosphoric acid. The amount of this acid naturally present in wines is 0·2–0·6 gram (P_2O_5) per litre. Addition of dicalcium phosphate is sometimes made to wine and in this case the proportion of P_2O_5 may be increased to 1·5 gram per litre, the ash also being considerably augmented.

Chlorides. These are present in wine in only small proportions—about 0·02–0·03 grams per litre, calculated as sodium chloride. With the object of increasing the savour of wine and of reviving the colour, as well as of disguising watering and raising the amount of ash, common salt is sometimes added. This is allowed to the extent of 1 gram of sodium chloride per litre.

It must, however, be noted that certain wines from salt regions or maritime districts may contain considerable quantities of sodium chloride. In these cases, the analytical results are compared with the composition of genuine wines from the same locality. After sea transport, wines sometimes contain sodium chloride as a result of infiltration of sea water through the walls of the containing vessels.

Nitrates. These are not usually present in wine, although they may occur in small quantities even in genuine wines. The existence of nitrates in a wine cannot, therefore, be attributed with certainty to addition of water containing nitrates, and thus has no absolute value as a criterion of watering. A marked reaction for nitrates may, however, be of value as indicating watering—which should be confirmed by other determinations—or may point to addition of nitric acid.

Antiseptics. In general, it is forbidden to treat wine with any antiseptic, excepting sulphurous acid in limited proportions.

Extraneous metals. Natural wines contain only minimal quantities of alumina—0·01–0·04 gram per litre—but the amount may be increased to as much as 0·2–0·3 gram per litre by treatment of the wine with substances containing alum.

Natural wines do not contain copper, lead, zinc, barium or strontium.

VINEGAR

Vinegar is prepared from a number of different materials and goes under the names of wine vinegar, malt vinegar, cider vinegar, glucose (or sugar) vinegar, spirit vinegar (from potato or cereal spirit), artificial vinegar (diluted, more or less pure acetic acid), etc., although these descriptions are not always justified by the origin of the product.

The better vinegars are adulterated in a number of ways, artificial vinegar, mineral acid, etc., being added. Coloration with caramel or artificial organic dyes is not uncommon, while treatment with flavouring agents, such as pepper, cayenne and ginger is also practised.

The following tests or a selection of them may be made :

1. External Properties.—The colour, clarity and odour are first noted. A turbid vinegar should be examined, if necessary with a lens or microscope, to ascertain if the turbidity is due to organisms (vinegar eels, etc.). The odour and taste are best observed by diluting the vinegar somewhat with tepid water, and should also be tested after the vinegar has been neutralised as exactly as possible with soda ; the latter test serves to indicate principally the presence of alcohol, aldehydes, or empyreumatic substances derived from pyroligneous acid. Lastly, the vinegar is diluted with water to ascertain if any turbidity is produced in this way.

2. Specific Gravity.—This is determined at 15° by means of the Westphal balance (*see* chapter on Spirits).

3. Extract.—50 c.c. of the vinegar are evaporated to a syrupy consistency in a platinum dish on a water-bath, the residue being taken up in 50 c.c. of water and again evaporated to a syrup. This addition of water and evaporation are again repeated twice with the object of expelling the acetic acid completely. The residue is then dried in a steam-oven for $2\frac{1}{2}$ hours, allowed to cool in a desiccator and weighed.

The colour, odour and solubility in water and alcohol of the extract obtained are noted.

4. Ash and Alkalinity of the Ash.—The methods given for wine are followed.

5. Acidity.—In general only the total acidity is determined; in some cases, however (for instance, when the vinegar contains other free acids than acetic), the fixed and volatile acidities are determined.

(*a*) TOTAL ACIDITY. 10–20 c.c. of the vinegar, measured exactly, are diluted with about an equal volume of water and titrated with N-sodium hydroxide in presence of a few drops of phenolphthalein. If the liquid is too highly coloured to allow the change of colour to be seen, either a greater amount of water is added or a drop of the liquid is withdrawn and tested with the indicator (*see* Wine, p. 191).

The acidity is expressed in grams of acetic acid per 100 c.c. (1 c.c. N–NaOH = 0·06 gram of acetic acid) or as percentage of acetic acid by weight.

Use is also made of special forms of apparatus, known as *acetimeters*, which admit of rapid and easy, if not very exact, determination of the total acidity of vinegar.

(*b*) FIXED ACIDITY. This is estimated on the residue from the distillation of the vinegar under reduced pressure,[1] this being carried out as follows:

Use is made of a flask *A* of about 150 c.c. capacity, furnished with a short side-tube and a bulb *B* holding about 50 c.c., and closed by a rubber stopper traversed by a tapped funnel *C* (about 20 c.c.), the stem of which reaches almost to the bottom of the flask (Fig. 57).

The flask *A* is immersed in a boiling water-bath and connected with a receiver, which is then evacuated by means of a water-pump. Exactly 5 c.c. of the vinegar are next introduced into the funnel, allowed to flow into the flask, and there distilled until the volume is reduced to 2–3 c.c.; without interruption of the operation, 20 c.c. of distilled water are then introduced and the volume again reduced to 2–3 c.c., two similar additions of distilled water being subsequently made. When the volume in the flask is finally reduced to about 5 c.c., the operation is stopped and the liquid transferred quantitatively into a conical flask, the fixed acidity being then determined by titration with N/10-sodium hydroxide either in presence of phenol-

FIG. 57

phthalein or, with a highly coloured residue, with the help of litmus paper.

The fixed acidity is usually expressed in grams of sulphuric acid per 100 c.c. of vinegar (1 c.c. N/10-NaOH = 0·0049 gram of H_2SO_4).

The distillate may be tested with silver nitrate to ascertain if any addition of hydrochloric acid has been made.

(*c*) VOLATILE ACIDITY. This is calculated by difference.
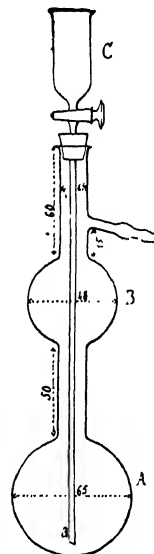
[1] Roos et Mestrezat; *Bull. de l'Assoc. des chim. de sucr.*, 1907–1908, p. 41.

6. Detection of Free Mineral Acids.—This may be effected by one of the following methods :

(*a*) WITH METHYL VIOLET. A little of the vinegar is diluted until its total acidity is about 2%, 20–25 c.c. of this liquid being treated with 4 or 5 drops of 0·01% methyl violet solution ; if the colour changes to blue or green, the presence of free mineral acid is indicated.

The coloration obtained should be compared with that produced by adding the same quantity of methyl violet solution to 20–25 c.c. of a 2% solution of pure acetic acid.

Highly coloured vinegars should be first treated with animal black which has been carefully washed with acid.

(*b*) BY DIALYSIS.[1] This serves in the case of coloured vinegars and is carried out as follows : 100 c.c. of the vinegar are boiled with 7–8 grams of finely powdered barium chloride,[2] 50 c.c. of the cooled liquid being heated to 50–60° and dialysed through *washed* parchment paper in a dialyser containing 50 c.c. of distilled water. After 5–10 minutes, 10 c.c. of the dialysate are withdrawn and tested with methyl violet as under (*a*). Medri, however, regards metanil yellow as more sensitive than methyl violet and takes 10–12 drops of a 0·1% solution of it for each test. In presence of mineral acid the lemon-yellow colour of the metanil yellow changes to orange-yellow or garnet-red or fuchsine-red or violet-red, according to the amount of the acid.

7. Determination of the Mineral Acid.—This may be carried out by the following slight modification of Schidrowitz's method [3] :

The method is based on the fact that slightly dissociated acids, such as acetic, tartaric, etc., do not exhibit their acidity towards methyl orange in presence of alcohol. If, then, a definite quantity of alkali is added to a genuine vinegar and the added alkali then neutralised in presence of methyl orange by means of an aqueous-alcoholic solution of sulphuric acid, the amount of the latter will correspond exactly with that of the alkali, since the acetic acid liberated from the acetate formed does not react with the indicator. If, however, a vinegar contains free mineral acid, the amount of sulphuric acid required will be diminished in accordance with the quantity of the alkali united with the free mineral acid ; the amount of the latter will thus correspond with the difference between the alkali added and the sulphuric acid necessary for its neutralisation.

When the liquid is coloured it is difficult to observe the change of colour of the indicator ; in such case, use is made of papers prepared by immersing filter-paper in a 0·1% methyl orange solution and drying in an oven.

The determination is carried out as follows : 5 c.c. of N/2-caustic soda are added to 20 c.c. of vinegar and the liquid evaporated to dryness. The residue is taken up in a mixture of 2 c.c. of water and 2 c.c. of absolute alcohol and the liquid titrated with an aqueous-alcoholic N/2-sulphuric

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[1] L. Medri : *Boll. chim. farmaceutico*, 1909, XLVIII, p. 331.

[2] The treatment with barium chloride is to precipitate any sulphuric acid present and to liberate from the barium chloride a corresponding amount of hydrochloric acid, which dialyses with much greater rapidity.

[3] *The Analyst*, 1903, XXVIII, p. 233.

acid solution, prepared by making 100 c.c. of the N-acid up to 200 c.c. with absolute alcohol; neutrality is reached when a drop of the liquid produces a reddish-brown spot on the methyl orange paper. If this occurs immediately the acid is added, the 5 c.c. of N/2-soda was insufficient to neutralise the free mineral acid present in the vinegar and the test must be repeated with a larger quantity. The free mineral acid corresponds with the volume of N/2-soda less that of N/2-sulphuric acid used: 1 c.c. N/2-NaOH = 0·0295 gram of H_2SO_4 or 0·0182 gram of HCl.

8. Phosphoric Acid.—This is determined on the ash, as in the case of wine (*q.v.*).

9. Detection and Determination of Extraneous Free Organic Acids.

(*a*) Oxalic Acid : 1. *Qualitative.* 50 c.c. of vinegar, rendered slightly alkaline with ammonia, are heated to boiling and treated with a slight excess of calcium sulphate; in presence of oxalic acid, a white crystalline precipitate of calcium oxalate is obtained.

2. *Quantitative.* The precipitate is filtered off, washed, ignited and weighed : 1 part of CaO = 2·25 parts of $H_2C_2O_4 + 2H_2O$.

(*b*) Tartaric Acid : 1. *Qualitative.* 100 c.c. of the vinegar are concentrated on the water-bath to a syrup, which is heated gently with alcohol and the solution filtered. A dilute alcoholic potassium hydroxide solution is added drop by drop to the filtrate, the walls of the vessel being rubbed meanwhile with a rod, the addition being continued until no further formation of precipitate takes place.

To ascertain if the precipitate is really cream of tartar, the following test, due to Dénigès, is used : When the crystalline precipitate has settled, the supernatant liquid is decanted off and the precipitate washed with a fine stream of alcohol into a dish, the excess of alcohol being then evaporated. Some of the remaining crystals are introduced into a test-tube containing 3 c.c. of concentrated sulphuric acid and 3 drops of a resorcinol solution prepared by dissolving 2 grams of pure resorcinol in 100 c.c. of water acidified with 5 c.c. of sulphuric acid. The solution is heated to 130–140° : in presence of tartaric acid, a distinct carmine coloration is produced.

2. *Quantitative* (total tartaric acid). 100 c.c. of the vinegar are treated in a beaker with 1 c.c. of 20% potassium acetate solution and 15 grams of powdered potassium chloride. When the latter has dissolved, 20 c.c. of 95% alcohol are added, the subsequent procedure being as indicated for the determination of the total tartaric acid in wine (*q.v.*, p. 193).

(*c*) Citric Acid. This is tested for by means of Dénigès reaction, as in wine (*see* p. 208).

10. Detection and Determination of the Alcohol.—1. *Qualitative.* 100 c.c. of the vinegar, neutralised exactly with sodium hydroxide (towards litmus paper), are distilled, the first 4–5 c.c. of distillate being tested for alcohol by Rimini's reaction (*see* Varnishes).

2. *Quantitative.* 400 c.c. of the vinegar, neutralised exactly with sodium hydroxide, are distilled, the first 200 c.c. of distillate being again distilled and 100 c.c. of distillate collected. From the density of this distillate the

nu 1 ber of grams of alcohol per 100 c.c. are determined (*see* p. 179) and thence the grams of alcohol per 100 c.c. of the vinegar.

11. Detection of Aldehydes.—100 c.c. of the vinegar are neutralised exactly with caustic soda and distilled, the first 10 c.c. of distillate being tested for aldehyde by means of Schiff's reagent (*see* p. 244).

12. Determination of the Glycerine.—As in wine (*q.v.*).

13. Determination of the Sugars (reducing substances).—*See* Wine, p. 194.

14. Detection of Heavy Metals.—200 c.c. of the vinegar, made alkaline with sodium carbonate and containing a little nitre, are evaporated, the residue incinerated and the ash examined by the ordinary analytical methods.

The following alternative procedure may also be used : 200 c.c. of the vinegar are evaporated to about 50 c.c. and then gently heated with 10 c.c. of concentrated hydrochloric acid, a few crystals of potassium chlorate being introduced from time to time until the liquid becomes colourless or only pale yellow. The excess of chlorine is expelled by boiling, the liquid being afterwards treated with 10 grams of sodium acetate, diluted to about 100 c.c. and subjected to the action of hydrogen sulphide. In presence of heavy metals, a precipitate is obtained which is analysed, particularly for copper, lead, tin and zinc, by the usual analytical methods.

15. Detection of Bisulphates.—The presence of bisulphates is revealed by the tests for free mineral acids and by analysis of the ash.

16. Detection of Pyrogenic Impurities.—The following tests serve mainly to detect the presence of pyroligneous acetic acid :

(*a*) 15–20 c.c. of the vinegar are neutralised with sodium hydroxide and heated on a water-bath : in presence of empyreumatic substances, a characteristic odour recalling that of smoke is observed.

(*b*) 100 c.c. of the vinegar are distilled, the first 10 c.c. of distillate being treated, gradually and with shaking, with 2 c.c. of 0·1% potassium permanganate solution. With genuine vinegar, the mixture remains coloured pink for at least 5 minutes ; if, however, the permanganate is immediately decolorised and considerably more is required to give a pink coloration persistent for 5 minutes, the presence of pyroligneous acetic acid is indicated.

17. Detection of Caramel.—This is carried out as with wine (*see* p. 202).

18. Detection of Artificial Organic Dyes.—As in wine.

19. Detection of Pungent Substances.—The presence of pungent substances (pepper, pimento, mustard, etc.) in vinegar is detected by neutralising 50 c.c. exactly, evaporating, and tasting the residue. To obtain more certain indications, the residue is extracted with ether, the ethereal solution evaporated and the residue then left tasted.

20. Detection of Preservatives.—Tests are made especially for salicylic acid, boric acid and formaldehyde, the methods given for wine being employed.

21. Detection of Dextrin.—The method used in the case of wine is used ; it serves to detect addition of glucose to the vinegar.

22. Distinction between Fermentation Vinegar and Wood Vinegar.—Wine vinegar may be characterised by its special aroma, by the presence

of bitartrate and glycerine, by the percentage and properties of the extract, by the proportion, composition and alkalinity of the ash, by the presence of small quantities of alcohol, aldehydes, etc.

Spirit vinegar is characterised by the presence of small amounts of alcohol and aldehydes, by the very small proportions of extract and ash— the latter being usually neutral and free from phosphates—and by the high ratio of acidity to extract.

Distilled vinegar (made artificially from acetic acid), besides by the absence of the elements characteristic of wine and spirit vinegars, is characterised by the small proportions of extract and ash, by the high ratio of acidity to extract and, if the acetic acid used were not sufficiently pure, by the presence of pyrogenic impurities.

There are also special reactions, based on the detection of fermentative bacteria or of their products, which serve to indicate the presence of fermentation vinegar ; these reactions naturally give positive results also when the fermentation vinegar is mixed with artificial vinegar. The most reliable of these reactions is that of Kraszewski [1] : 100 c.c. of the vinegar, rendered alkaline with sodium hydroxide, are shaken (gently, to avoid the formation of an emulsion) in a separating funnel with amyl alcohol. The latter is afterwards decanted off and evaporated, the residue being taken up in a little water and the solution acidified with dilute sulphuric acid and treated with a few drops of a solution of iodine in potassium iodide. In presence of fermentation vinegar, a slight precipitate or a turbidity is formed.

23. Detection of Denatured Alcohol.—As in spirits (q.v.).

24. Detection and Estimation of Arsenic.—As in beer (q.v.).

* * *

Wine vinegar is yellowish-white or wine-red according to the colour of the original wine, and it has a pleasant ethereal odour due to the esters formed during fermentation and a distinctly acid, but not acrid or repulsive, taste. Its density varies from 1·015 to 1·020, and its total *acidity* lies, for good vinegars, between 6 and 8 grams of acetic acid per 100 c.c. ; weak vinegars are, however, sold having acidities as low as 4 grams per 100 c.c. The *extract* left on evaporation varies from 1·2 to 2·2 grams per 100 c.c. and resembles that of wine. The *ash* amounts to 0·12–0·35 gram per 100 c.c., contains phosphates and has an *alkalinity* of 1·06–4·52 c.c. of N-alkali per 100 c.c. The *ratio of acidity to extract* may attain a maximum of 5·6 for vinegar from red wine or 7·9 for that from white wine.

Wine vinegar usually contains also small quantities of untransformed *alcohol* (about 1%), *glycerine* (0·2–0·75 gram per 100 c.c.), potassium bitartrate, nitrogenous substances and aldehydes, together with traces of chlorides, sulphates and lime.

Spirit vinegar is originally colourless, but it is generally coloured with caramel or with artificial organic dyes to render it more closely similar to wine vinegar. It smells of acetic acid and has a strongly acid taste, but lacks the characteristic aroma of genuine wine vinegar. Its density is about 1·010. When evaporated it leaves very little *extract* (0·2–0·6 gram per 100 c.c.), which yields but traces of *ash* (0·02–0·06 gram per 100 c.c.), this being usually neutral and free from phosphates. The *ratio of acidity to extract* is much higher than with wine vinegar

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[1] *Zeitschr. Nahr- und Genuss-mittel*, 1906, I, p. 386.

(10–30 or even more). The *acidity*, expressed as acetic acid, varies from 6 to 9 grams per 100 c.c. As in wine vinegar, small proportions of alcohol and aldehydes are present.

Artificial vinegar, obtained by dilution of acetic acid (wood vinegar) is also colourless of itself but is usually coloured artificially. It is devoid of aroma and has an unpleasant, burning, acid taste. Its *density* lies between 1·035 and 1·060 and the weight of *extract* between 0·15 and 0·26 gram per 100 c.c.; very little *ash* is left. If the acetic acid used were impure (pyroligneous acetic acid), the characteristic empyreumatic odour is observed when the neutralised vinegar is evaporated, while the distillate yielded by the vinegar absorbs considerable quantities of permanganate; these characters may be lacking when the acetic acid has been sufficiently purified (especially by means of permanganate). Artificial vinegar does not give the Kraszewski reaction characteristic of fermentation vinegar.

Whatever its origin, *good comestible vinegar* should be clear and free from mineral acids, other organic acids than acetic, pungent substances, metals, preservatives and pyrogenic impurities. Artificial colouring is allowable, provided it is attained with harmless colouring matters.

Chapter VII

SPIRITS AND LIQUEURS

Spirits occurring in commerce may be distinguished as *industrial* and *potable spirits*. The former are *crude* if obtained directly by distillation of the products of fermentation, *rectified* if they have been subjected to further treatment for purification, or *denatured* if containing substances which render them unusable for drinking. Potable spirits are given special names according to the nature of the raw materials from which they are prepared. Thus, *brandy* is obtained by distillation of wine (*cognac*) or wine lees or marc (*eau de vie*), *rum* from cane-sugar molasses, *kirschwasser* from cherries, *whisky* from cereals, etc.

Rectified spirit is also used for the manufacture of *liqueurs*, by addition of various substances, such as natural or artificial essences, sugars, bitter principles, etc.

The tests to be made on spirits and liqueurs include a certain number which are common to all these products, such as determinations of the alcoholic strength, extract and ash, and tests for impurities and denaturing agents; other investigations are made only with certain products, examples of these being the examination of kirschwasser for hydrocyanic acid, the determination of sugars in liqueurs, etc. The former are treated under *General Methods* and the latter in the *Special Part*.

The results are expressed as follows: Alcohol in percentage by volume to two decimal figures; extract, sugars and ash in grams per litre to two decimal figures; impurities of the alcohol in milligrams per 100 c.c. of anhydrous alcohol; the free and combined hydrocyanic acid and benzaldehyde in milligrams per litre to the nearest milligram.

Sampling.—Whatever the product to be examined, sampling is of the utmost importance. The sample should be taken from the vessels or casks after the mass has been well mixed or it should be drawn in portions from different levels by means of special siphons.[1] If the product is distributed between several casks, quantities from each proportional to the contents should be mixed. It is, however, always preferable, especially when there is no absolute certainty as to the identity of the products in the different vessels, to take a separate sample from each and to indicate the quantity represented by each sample.

The amount of liquid necessary for analysis varies according to the determinations required; in general 0·5–1 litre is sufficient. Each sample should be stored in a clean, dry bottle, which is filled and then tightly closed.

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[1] This is absolutely necessary, especially when the spirits are contained in large vessels holding many hectolitres, since layers form which may vary in specific gravity and hence in alcoholic strength.

GENERAL METHODS

1. Objective Characters

Observation should be made of the colour, brightness, smell and taste of the sample   Of especial importance is tasting, which, to an expert, may give valuable indications concerning the quality of the product.

In judging of the smell and taste of an alcoholic liquid, the following procedure is to be recommended.   Into a conical flask of about 200 c.c. capacity [1] are poured a few c.c. (20–25) of the liquid and sufficient tepid water to bring the strength to about 30% by volume, the flask being closed and shaken and then opened and smelt.   A little of the tepid liquid is held in the mouth for a few moments and then rejected, the impression on the palate both during and after contact with the liquid being noted.   More certain results are obtained if comparison is made with a standard spirit.

Only with practice is it possible to judge of the greater or less purity of the alcohol, of the nature of the predominant impurities and of the special aromas characteristic of the different products.

Another method of testing consists in pouring a small quantity of the liquid into a glass, the walls being moistened and the excess then eliminated ; the glass is then covered with a sheet of paper and left until the following day.   Added perfumes in particular may be detected in this way.

When liqueurs or other products rich in extraneous matters are to be examined, it is convenient to taste both the product itself and also its distillate—freed, if necessary, from essential oils—in order to arrive at a decision as to the quality of the alcohol used in the manufacture.

2. Determination of the Alcohol

The quantity of alcohol contained in spirits, i.e., the *alcoholic strength*, is determined either indirectly from the specific gravity or directly by means of alcoholometers.

With a product containing no appreciable amount of fixed matters (which may be detected by evaporating a little of the material in a dish on the water-bath) and no considerable quantity of volatile matters other than ethyl alcohol and water, such as volatile acids and bases and essential oils, the specific gravity is taken on the liquid as it stands.   With a spirit containing appreciable quantities of extraneous substances it is, however, necessary first to eliminate these by the following preliminary treatment.

1. Preliminary Treatment.—When the extraneous matters are fixed (extracts, sugars, etc.) or are volatile acids or alkalies, method (*A*) is used, whereas when they are essential oils, procedure (*B*) is employed.

(*A*) IN PRESENCE OF FIXED MATTERS.   Two cases present themselves, according as volatile acids or alkalies are present or absent.

(1) If the liquid is free from volatile acids or alkalies and does not contain more than about 60% of alcohol (by volume), a 100 or 200 c.c.

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[1] In practice, special glasses widened at the base and cylindrical in the upper part are used for tasting.

flask is filled almost up to the mark, then placed for some time in a water-bath at 15° C. and finally made exactly up to the mark. The liquid and the rinsings of the flask with distilled water are introduced into a larger flask which is connected with a condenser, at least three-fourths of the liquid being distilled over into the original measuring flask ; the distillate is brought to 15° C. and made up to the mark with distilled water. The specific gravity of this liquid is then determined.

If the liquid contains more than 60% of alcohol, 100 c.c. of it are diluted to about double the volume and the distillate made up to 200 c.c. with distilled water. The specific gravity is then determined as before.

(2) When volatile acid or alkali is present, this is neutralised exactly with dilute caustic alkali or sulphuric acid, the subsequent procedure being as described above.

(B) IN PRESENCE OF VOLATILE OILS. These may be expelled as follows :

(1) In a separating funnel, 50 c.c. of the liquid are shaken carefully, so as to avoid emulsification, with 100 c.c. of 10% sodium chloride solution and 100 c.c. of vaseline oil. After a rest of a few minutes, the liquid is again cautiously shaken ; this operation is repeated three or four times, the liquid being finally left until the two layers separate completely. The lower alcoholic liquid is allowed to flow into a conical flask and the vaseline oil washed several times with fresh sodium chloride solution, about 75 c.c. of the latter being used. This washing liquid is placed in the flask with the alcoholic liquid and the whole distilled, the distillate being collected in a 200 c.c. measuring flask. The distillate is made up to volume and its specific gravity determined, the quantity of alcohol calculated, multiplied by four, giving the alcoholic content of the liquid.

(2) The alcoholic liquid is diluted until its apparent alcoholic strength is about 30% by volume. Of the liquid thus obtained, 100 c.c. are shaken with 100 c.c. of mineral oil (obtained by collecting the fractions of Russian petroleum which boil at 140-230° and have the sp. gr. about 0·812), the aqueous alcoholic layer being separated after standing. The petroleum is washed a couple of times with a little water (about 25 c.c. each time), which is mixed with the aqueous alcoholic liquid ; the latter is then distilled twice, the distillate being made up to 100 c.c. The specific gravity of the distillate gives the exact strength of the liquid diluted to about 30%, so that, the dilution being known, the strength of the original liquid is readily deduced.

Elimination of the volatile oils is not usually necessary, but is required only with certain special products, such as essences for liqueurs, which give a distillate turning turbid and depositing small oily drops on dilution with water.

2. Determination of the Alcoholic Strength from the Specific Gravity.—The specific gravity of the alcoholic liquid is first determined by means of the apparatus here described and the alcoholic strength then deduced as described later (p. 236).

(1) APPARATUS AND METHODS OF USING THEM. Use is generally made of the Westphal balance or the picnometer.

(a) *Westphal balance.* This consists of a hydrostatic balance (**Fig.**

58), the column being formed of two parts, one movable inside the other so that it may be raised or lowered at will. It may be rendered perfectly vertical by means of a screw, the point of which forms one of the three feet of the base of the column. The latter carries at the top a support furnished with a double inclined steel plane on which rests, by means of a knife-edge, a beam with unequal arms. The shorter arm is the thicker and heavier and terminates in a cylindrical swelling provided with a point which, when the beam is in equilibrium, corresponds exactly with another point fixed to the stand. At the end of the longer and lighter arm is a hook to which can be hung, by means of a fine platinum wire, a cylindrical glass float usually containing a thermometer ; this arm is divided, between the point of support and the point at which the float is suspended, into ten equal parts, marked by notches. The dimensions and weights of the different parts of the apparatus are so regulated that, when the column is absolutely vertical and the float attached to the hook, the beam is in equilibrium. To make the column vertical, use is made of the screw which forms one of the feet and should be in the same plane as the beam, as shown in the figure.
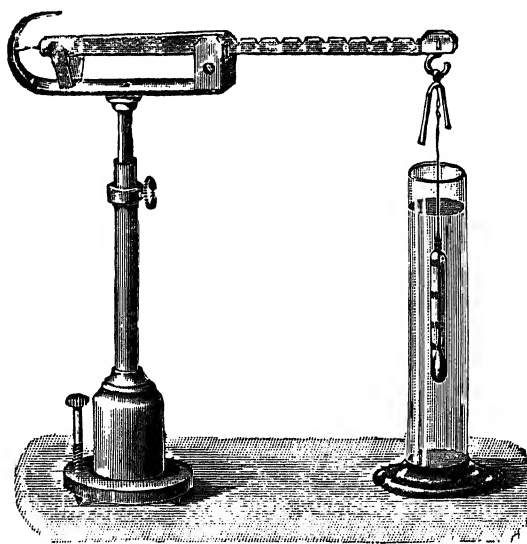
FIG. 58

If now the float is immersed in a liquid, the equilibrium is disturbed, and to re-establish it a series of riders the weights of which are in the proportions 1000, 100, 10 and 1, are placed at the proper positions on the graduated arm. One of the weights of the first of these magnitudes is equal to the weight of distilled water at 15° C.[1] displaced by the float, so that, when attached at the end of the arm, it will restore equilibrium when the float is immersed in water at this temperature. When a liquid other than water is used, equilibrium is re-established by placing the different weights, beginning with the heaviest, at different positions on the beam ; with a liquid heavier than water (i.e., with sp. gr. between 1 and 2), one of the weights of the first magnitude is always placed at the end of the arm.

If equilibrium is attained when the weights of the four magnitudes occupy respectively the eighth, ninth, fifth and eighth divisions of the beam, the specific gravity of the liquid at 15°/15° will be 0·8958. If two weights of the first magnitude are placed one at the end and the other at the second division, and one

[1] Westphal balances are sometimes graduated at other normal temperatures, e.g., 17·5° or 20°, according to the purposes for which they are intended.

each of the second and fourth magnitudes at the seventh and fifth divisions respectively, the sp. gr. will be 1·2705.

Before the Westphal balance is used, the screwed foot (found on the side of the shorter arm) should be regulated so that the pillar is vertical, this being shown by the beam being in equilibrium when the float hangs from the hook in the air. To test the accuracy of the instrument and weights, the float is immersed in distilled water at the normal temperature [1]; equilibrium should then be restored by each of the heaviest weights hung in turn at the extremity of the arm. Equilibrium should also be maintained by two of the weights of the second magnitude placed respectively at the ninth and first divisions, or the eighth and second, or the seventh and third, or the sixth and fourth, or both at the fifth division (one hung on the curved extremity of the other). Equilibrium should also be attained (1) with a weight of the first magnitude at division 9 and one of the second magnitude at the end of the arm, (2) with both these at division 9 and a weight of the third magnitude at the end, or (3) with all three at division 9 and a weight of the fourth magnitude at the end.

Care should always be taken that the float is equally immersed, the twisted part of the platinum wire and the same length of the latter being below the surface in the position of equilibrium; no air-bubbles should be adherent to the float. In making an observation, the beam is allowed to oscillate freely; when it comes to rest, the fixed and movable points should correspond exactly.

When the float of a Westphal balance is replaced, the new float should have exactly the same weight as the old and since the magnitudes of the rider weights depend on the volume of the float, the series of weights must be changed at the same time. This may be avoided by using Reimann's floats, which have a fixed and definite weight and volume; the ordinary type has, with the suspension wire, a weight of 15 grams and displaces 5 grams of distilled water at the normal temperature, the weights being 5, 0·5, 0·05 and 0·005 grams respectively.

(b) *Picnometers*. These consist of glass vessels with narrow necks marked at a certain point. The picnometer is weighed empty, then filled with water up to the mark and finally filled with the liquid concerned. Before adjusting the liquid exactly to the mark, the picnometer is kept at the proper temperature (for spirits usually 15°) for a time sufficient to ensure the assumption of this temperature by the liquid. If P, P' and P'' are the weights thus found, the specific gravity of the liquid is:

$$\frac{P'' - P}{P' - P}.$$

Exact determinations, even with small quantities of liquid, may be made with Sprengel's picnometer, consisting of a U-tube terminated by two capillary tubes bent at right angles; one of these tubes—the less narrow—is furnished with a mark. This is filled by applying suction at

[1] To determine the temperature of the liquid accurately it is best to use, not the thermometer contained in the float, but a separate tested thermometer, which should indicate fifths or tenths of a degree.

TABLE XXIV

Determination of the Alcoholic Strength from the Specific Gravity

Specific Gravity at 15°/15°.	Alcohol % by Weight.	Alcohol % by Volume.	Grams of Alcohol per 100 c.c.	Specific Gravity at 15°/15°.	Alcohol % by Weight.	Alcohol % by Volume.	Grams of Alcohol per 100 c.c.	Specific Gravity at 15°/15°.	Alcohol % by Weight.	Alcohol % by Volume.	Grams of Alcohol per 100 c.c.
0·9710	20·52	25·08	19·91	0·9460	36·75	43·77	34·73	0·9210	48·93	56·74	45·03
0·9705	20·92	25·56	20·28	0·9455	37·01	44·06	34·96	0·9205	49·16	56·97	45·21
0·9700	21·32	26·03	20·66	0·9450	37·28	44·35	35·20	0·9200	49·39	57·21	45·40
0·9695	21·71	26·50	21·03	0·9445	37·54	44·64	35·43	0·9195	49·61	57·44	45·58
0·9690	22·10	26·96	21·40	0·9440	37·80	44·93	35·66	0·9190	49·84	57·67	45·76
0·9685	22·49	27·42	21·76	0·9435	38·07	45·22	35·88	0·9185	50·07	57·90	45·95
0·9680	22·87	27·87	22·12	0·9430	38·33	45·50	36·11	0·9180	50·29	58·13	46·13
0·9675	23·25	28·32	22·47	0·9425	38·59	45·79	36·34	0·9175	50·52	58·36	46·31
0·9670	23·63	28·76	22·82	0·9420	38·84	46·07	36·56	0·9170	50·75	58·59	46·49
0·9665	24·00	29·20	23·17	0·9415	39·10	46·35	36·78	0·9165	50·97	58·82	46·67
0·9660	24·37	29·64	23·52	0·9410	39·35	46·63	37·00	0·9160	51·20	59·05	46·86
0·9655	24·73	30·06	23·86	0·9405	39·61	46·90	37·22	0·9155	51·42	59·27	47·04
0·9650	25·09	30·49	24·19	0·9400	39·86	47·18	37·44	0·9150	51·65	59·50	47·22
0·9645	25·45	30·91	24·53	0·9395	40·11	47·45	37·66	0·9145	51·87	59·72	47·39
0·9640	25·81	31·32	24·85	0·9390	40·37	47·72	37·87	0·9140	52·09	59·95	47·57
0·9635	26·16	31·73	25·18	0·9385	40·62	47·99	38·09	0·9135	52·32	60·17	47·75
0·9630	26·51	32·14	25·50	0·9380	40·87	48·26	38·30	0·9130	52·54	60·40	47·93
0·9625	26·85	32·54	25·82	0·9375	41·11	48·53	38·51	0·9125	52·76	60·62	48·11
0·9620	27·19	32·93	26·13	0·9370	41·36	48·80	38·72	0·9120	52·99	60·84	48·28
0·9615	27·53	33·33	26·45	0·9365	41·61	49·06	38·93	0·9115	53·21	61·06	48·46
0·9610	27·86	33·71	26·75	0·9360	41·85	49·33	39·14	0·9110	53·43	61·29	48·64
0·9605	28·19	34·10	27·06	0·9355	42·10	49·59	39·35	0·9105	53·65	61·51	48·81
0·9600	28·52	34·47	27·36	0·9350	42·34	49·85	39·56	0·9100	53·88	61·73	48·99
0·9595	28·85	34·85	27·66	0·9345	42·59	50·11	39·76	0·9095	54·10	61·95	49·16
0·9590	29·17	35·22	27·95	0·9340	42·83	50·37	39·97	0·9090	54·32	62·17	49·33
0·9585	29·49	35·59	28·24	0·9335	43·07	50·62	40·17	0·9085	54·54	62·39	49·51
0·9580	29·81	35·95	28·53	0·9330	43·31	50·88	40·38	0·9080	54·76	62·61	49·68
0·9575	30·12	36·31	28·82	0·9325	43·55	51·14	40·58	0·9075	54·98	62·82	49·86
0·9570	30·43	36·67	29·10	0·9320	43·79	51·39	40·78	0·9070	55·20	63·04	50·03
0·9565	30·74	37·02	29·38	0·9315	44·03	51·64	40·98	0·9065	55·43	63·26	50·20
0·9560	31·05	37·37	29·66	0·9310	44·27	51·89	41·18	0·9060	55·65	63·47	50·37
0·9555	31·36	37·72	29·93	0·9305	44·51	52·14	41·38	0·9055	55·87	63·69	50·54
0·9550	31·66	38·06	30·21	0·9300	44·75	52·39	41·58	0·9050	56·09	63·91	50·71
0·9545	31·96	38·40	30·48	0·9295	44·98	52·64	41·78	0·9045	56·31	64·12	50·89
0·9540	32·25	38·74	30·74	0·9290	45·22	52·89	41·97	0·9040	56·52	64·34	51·06
0·9535	32·55	39·07	31·01	0·9285	45·46	53·14	42·17	0·9035	56·74	64·55	51·23
0·9530	32·84	39·40	31·27	0·9280	45·69	53·39	42·37	0·9030	56·96	64·76	51·39
0·9525	33·13	39·73	31·53	0·9275	45·93	53·63	42·56	0·9025	57·18	64·98	51·56
0·9520	33·42	40·06	31·79	0·9270	46·16	53·88	42·76	0·9020	57·40	65·19	51·73
0·9515	33·71	40·38	32·05	0·9265	46·39	54·12	42·95	0·9015	57·62	65·40	51·90
0·9510	33·99	40·70	32·30	0·9260	46·63	54·36	43·14	0·9010	57·84	65·61	52·07
0·9505	34·28	41·02	32·55	0·9255	46·86	54·60	43·33	0·9005	58·06	65·82	52·24
0·9500	34·56	41·33	32·80	0·9250	47·09	54·84	43·52	0·9000	58·27	66·03	52·40
0·9495	34·84	41·64	33·05	0·9245	47·32	55·08	43·71	0·8995	58·49	66·24	52·57
0·9490	35·11	41·95	33·30	0·9240	47·55	55·32	43·90	0·8990	58·71	66·45	52·74
0·9485	35·39	42·26	33·54	0·9235	47·78	55·56	44·09	0·8985	58·93	66·66	52·90
0·9480	35·66	42·57	33·78	0·9230	48·01	55·80	44·28	0·8980	59·15	66·87	53·07
0·9475	35·94	42·87	34·02	0·9225	48·24	56·03	44·47	0·8975	59·36	67·08	53·23
0·9470	36·21	43·17	34·26	0·9220	48·47	56·27	44·65	0·8970	59·58	67·29	53·40
0·9465	36·48	43·47	34·50	0·9215	48·70	56·50	44·84	0·8965	59·80	67·50	53·56

TABLE XXIV—*continued*

Specific Gravity at 15°/15°.	Alcohol % by Weight.	Alcohol % by Volume.	Grams of Alcohol per 100 c.c.	Specific Gravity at 15°/15°.	Alcohol % by Weight.	Alcohol % by Volume.	Grams of Alcohol per 100 c.c.	Specific Gravity at 15°/15°.	Alcohol % by Weight.	Alcohol % by Volume.	Grams of Alcohol per 100 c.c.
0·8960	60·02	67·70	53·73	0·8700	71·12	77·90	61·82	0·8440	81·83	86·95	69·00
0·8955	60·23	67·91	53·89	0·8695	71·33	78·08	61·97	0·8435	82·03	87·11	69·13
0·8950	60·45	68·12	54·05	0·8690	71·54	78·27	62·11	0·8430	82·23	87·28	69·26
0·8945	60·66	68·32	54·22	0·8685	71·74	78·45	62·26	0·8425	82·43	87·44	69·39
0·8940	60·88	68·53	54·38	0·8680	71·95	78·64	62·40	0·8420	82·63	87·60	69·52
0·8935	61·10	68·73	54·54	0·8675	72·16	78·82	62·55	0·8415	82·83	87·76	69·64
0·8930	61·31	68·94	54·71	0·8670	72·37	79·00	62·69	0·8410	83·03	87·92	69·77
0·8925	61·53	69·14	54·87	0·8665	72·58	79·18	62·84	0·8405	83·23	88·08	69·90
0·8920	61·75	69·34	55·03	0·8660	72·79	79·37	62·98	0·8400	83·43	88·23	70·02
0·8915	61·96	69·55	55·19	0·8655	73·00	79·55	63·13	0·8395	83·63	88·39	70·15
0·8910	62·18	69·75	55·35	0·8650	73·21	79·73	63·27	0·8390	83·83	88·55	70·27
0·8905	62·39	69·95	55·51	0·8645	73·42	79·91	63·41	0·8385	84·03	88·71	70·40
0·8900	62·61	70·16	55·67	0·8640	73·63	80·09	63·56	0·8380	84·22	88·86	70·52
0·8895	62·82	70·36	55·83	0·8635	73·83	80·27	63·70	0·8375	84·42	89·02	70·65
0·8890	63·04	70·56	55·99	0·8630	74·04	80·45	63·85	0·8370	84·62	89·18	70·77
0·8885	63·25	70·76	56·15	0·8625	74·25	80·63	63·99	0·8365	84·82	89·33	70·89
0·8880	63·47	70·96	56·31	0·8620	74·46	80·81	64·13	0·8360	85·01	89·48	71·01
0·8875	63·68	71·16	56·47	0·8615	74·67	80·99	64·27	0·8355	85·21	89·64	71·14
0·8870	63·90	71·36	56·63	0·8610	74·87	81·17	64·41	0·8350	85·41	89·79	71·26
0·8865	64·11	71·56	56·79	0·8605	75·08	81·34	64·55	0·8345	85·60	89·94	71·38
0·8860	64·33	71·76	56·94	0·8600	75·29	81·52	64·69	0·8340	85·80	90·09	71·50
0·8855	64·54	71·96	57·10	0·8595	75·50	81·70	64·84	0·8335	85·99	90·24	71·62
0·8850	64·75	72·15	57·26	0·8590	75·70	81·87	64·97	0·8330	86·19	90·40	71·74
0·8845	64·97	72·35	57·42	0·8585	75·91	82·05	65·11	0·8325	86·38	90·55	71·85
0·8840	65·18	72·55	57·57	0·8580	76·12	82·23	65·25	0·8320	86·58	90·70	71·97
0·8835	65·40	72·74	57·73	0·8575	76·32	82·40	65·39	0·8315	86·77	90·84	72·09
0·8830	65·61	72·94	57·88	0·8570	76·53	82·57	65·53	0·8310	86·97	90·99	72·21
0·8825	65·82	73·14	58·04	0·8565	76·74	82·75	65·67	0·8305	87·16	91·14	72·33
0·8820	66·04	73·33	58·19	0·8560	76·94	82·92	65·81	0·8300	87·35	91·29	72·44
0·8815	66·25	73·53	58·35	0·8555	77·15	83·10	65·94	0·8295	87·55	91·43	72·56
0·8810	66·46	73·72	58·50	0·8550	77·35	83·27	66·08	0·8290	87·74	91·58	72·67
0·8805	66·67	73·92	58·66	0·8545	77·56	83·44	66·22	0·8285	87·93	91·72	72·79
0·8800	66·89	74·11	58·81	0·8540	77·76	83·61	66·36	0·8280	88·12	91·87	72·90
0·8795	67·10	74·30	58·96	0·8535	77·97	83·78	66·49	0·8275	88·31	92·01	73·02
0·8790	67·31	74·49	59·12	0·8530	78·17	83·96	66·63	0·8270	88·50	92·15	73·13
0·8785	67·52	74·69	59·27	0·8525	78·38	84·13	66·76	0·8265	88·69	92·30	73·24
0·8780	67·74	74·88	59·42	0·8520	78·58	84·30	66·90	0·8260	88·88	92·44	73·36
0·8775	67·95	75·07	59·57	0·8515	78·79	84·47	67·03	0·8255	89·07	92·58	73·47
0·8770	68·16	75·26	59·73	0·8510	78·99	84·64	67·16	0·8250	89·26	92·72	73·58
0·8765	68·37	75·45	59·88	0·8505	79·20	84·80	67·30	0·8245	89·45	92·86	73·69
0·8760	68·58	75·64	60·03	0·8500	79·40	84·97	67·43	0·8240	89·64	93·00	73·80
0·8755	68·80	75·84	60·18	0·8495	79·60	85·14	67·57	0·8235	89·83	93·14	73·91
0·8750	69·01	76·02	60·33	0·8490	79·81	85·31	67·70	0·8230	90·02	93·28	74·02
0·8745	69·22	76·21	60·48	0·8485	80·01	85·47	67·83	0·8225	90·20	93·41	74·13
0·8740	69·43	76·40	60·63	0·8480	80·21	85·64	67·96	0·8220	90·39	93·55	74·24
0·8735	69·64	76·59	60·78	0·8475	80·42	85·81	68·09	0·8215	90·58	93·68	74·35
0·8730	69·85	76·78	60·93	0·8470	80·62	85·97	68·23	0·8210	90·76	93·82	74·45
0·8725	70·06	76·97	61·08	0·8465	80·82	86·14	68·36	0·8205	90·95	93·95	74·56
0·8720	70·27	77·15	61·23	0·8460	81·02	86·30	68·49	0·8200	91·13	94·09	74·66
0·8715	70·48	77·34	61·38	0·8455	81·22	86·46	68·62	0·8195	91·32	94·22	74·77
0·8710	70·70	77·53	61·52	0·8450	81·43	86·63	68·75	0·8190	91·50	94·35	74·87
0·8705	70·91	77·71	61·67	0·8445	81·63	86·79	68·88	0·8185	91·68	94·48	74·98

TABLE XXIV—*continued*

Specific Gravity at 15°/15°.	Alcohol % by Weight.	Alcohol % by Volume.	Grams of Alcohol per 100 c.c.	Specific Gravity at 15°/15°.	Alcohol % by Weight.	Alcohol % by Volume.	Grams of Alcohol per 100 c.c.	Specific Gravity at 15°/15°.	Alcohol % by Weight.	Alcohol % by Volume.	Grams of Alcohol per 100 c.c.
0·8180	91·87	94·61	75·08	0·8095	94·90	96·73	76·76	0·8015	97·63	98·52	78·19
0·8175	92·05	94·75	75·19	0·8090	95·08	96·85	76·86	0·8010	97·80	98·63	78·27
0·8170	92·23	94·87	75·29	0·8085	95·25	96·96	76·95	0·8005	97·97	98·74	78·36
0·8165	92·41	95·00	75·39	0·8080	95·43	97·08	77·04	0·8000	98·13	98·84	78·44
0·8160	92·59	95·13	75·49	0·8075	95·60	97·19	77·13	0·7995	98·30	98·95	78·52
0·8155	92·77	95·26	75·59	0·8070	95·77	97·31	77·24	0·7990	98·46	99·05	78·61
0·8150	92·96	95·38	75·69	0·8065	95·94	97·42	77·31	0·7985	98·63	99·15	78·69
0·8145	93·13	95·51	75·79	0·8060	96·11	97·54	77·40	0·7980	98·79	99·26	78·77
0·8140	93·31	95·63	75·89	0·8055	96·29	97·65	77·49	0·7975	98·95	99·36	78·85
0·8135	93·49	95·76	75·99	0·8050	96·46	97·76	77·58	0·7970	99·11	99·46	78·93
0·8130	93·67	95·88	76·09	0·8045	96·63	97·87	77·67	0·7965	99·28	99·56	79·01
0·8125	93·85	96·00	76·19	0·8040	96·79	97·99	77·76	0·7960	99·44	99·66	79·08
0·8120	94·03	96·13	76·29	0·8035	96·96	98·09	77·85	0·7955	99·60	99·76	79·16
0·8115	94·20	96·25	76·38	0·8030	97·13	98·20	77·93	0·7950	99·76	99·86	79·24
0·8110	94·38	96·37	76·48	0·8025	97·30	98·31	78·02	0·7945	99·92	99·95	79·32
0·8105	94·55	96·49	76·57	0·8020	97·47	98·42	78·10	0·7925	100·00	100·00	79·36
0·8100	94·73	96·61	76·67								

the narrower of the two tubes, while the other is immersed in the liquid. Filter paper is then carefully applied at the end of the narrow tube so that the latter remains full of the liquid, which is drawn to the mark in the wider tube.   The two ends of the tubes are then covered with small ground caps.

2. CALCULATION OF THE ALCOHOLIC STRENGTH FROM THE SPECIFIC GRAVITY.   The alcoholic strength is now deduced from the specific gravity by means of suitable tables.   Those commonly used are calculated for specific gravities at 15° C. referred to water at the same temperature and from these Table XXIV is deduced.   The part of the table which refers to alcoholic liquids containing up to 26% of alcohol by volume and is used especially for beer and wine, is given in full (i.e., for specific gravities differing by only 0·0001) in the chapter dealing with wine (*see* Table XXI, pp. 179 *et seq.*).

The second column of Table XXIV gives the percentage of alcohol by weight (grams of alcohol in 100 grams) in aqueous alcohol of the specific gravity shown in the first column; the third column gives the number of c.c. of alcohol in 100 c.c. and the fourth the number of grams of alcohol in 100 c.c.

If the specific gravity is determined directly on the liquid, the table gives directly the percentages of alcohol.   If, however, it is determined on the distillate made up to the original volume, the percentage of alcohol by volume and the number of grams of alcohol in 100 c.c. are read off directly, these numbers being doubled when the distillate is made up to twice the original volume.   The percentage of alcohol by weight in the original liquid

is found by determining the specific gravity s of the latter at $15°/15°$ and applying the formula :

$$x = \frac{k\,g}{0 \cdot 999154\,s},$$

where g is the number of grams of alcohol in 100 c.c. of the distillate, k the dilution of the latter, $0 \cdot 999154$ the weight in grams of 1 c.c. of water at $15°$ C. and x the required percentage of alcohol by weight in the liquor under examination.

3. Direct Determination of the Alcoholic Strength by means of the Alcoholometer.—In practice the determination of the specific gravity and the use of tables are avoided by direct determination of the alcoholic strength by means of hydrometers with suitable graduation known as *alcoholometers*.

The one most commonly used is that of *Gay-Lussac* which is graduated at $15°$ C. and gives the alcoholic strength by volume (number of c.c. of alcohol in 100 c.c. of the liquid at $15°$ C.). In Italy and certain other countries, the official alcoholometer is that of *Tralles*; this differs from the preceding only in being graduated at $15 \cdot 56°$ C. ($60°$ F.), so that its indications differ from those of the Gay-Lussac alcoholometer.[1]

The alcoholometer should be carefully cleaned and dried and then gradually immersed in the liquid contained in a cylindrical vessel and maintained at the required temperature ; it should be gently agitated to detach any adherent air-bubbles. It is

FIG. 59

then left to itself and when equilibrium has been attained, the reading on the stem corresponding with the level surface of the liquid (*see* Fig. 59) is determined.

When the alcoholometric determination is made at a temperature other than that for which the instrument is graduated, the readings require corrections, which are taken from tables which have been compiled.

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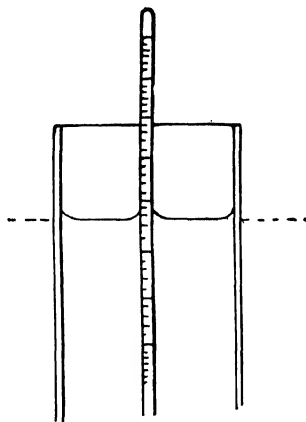
[1] In Great Britain and Ireland, and in most British colonies, the strength of spirit is often expressed in relation to that of so-called *proof spirit*, namely, " that which at the temperature of $51°$ F. weighs exactly twelve-thirteenths of an equal measure of distilled water " at the same temperature. Proof spirit contains $49 \cdot 28\%$ by weight or $57 \cdot 10\%$ by volume of absolute alcohol and has the specific gravity $0 \cdot 91976$ at $15 \cdot 6°/15 \cdot 6°$ C. A spirit is said to be 25 degrees under proof when 100 vols. of it contain 75 vols. of proof spirit or 25 degrees over proof when 100 vols. of it yield 125 vols. of proof spirit on dilution with water. If W and V represent the percentages of absolute alcohol by weight and volume respectively, P the percentage of proof spirit and D the specific gravity, the following relations hold :

$$P = V \times 1 \cdot 7525, \text{ or } V = P \times 0 \cdot 5706$$
$$V = W\,D \times 1 \cdot 26, \text{ or } W = (V \times 0 \cdot 7938) \div D$$
$$P = W\,D \times 2 \cdot 208, \text{ or } W = (P \times 0 \cdot 453) \div D$$

The official alcoholometer is the Sikes' hydrometer, which is a gilded brass instrument and is provided with a number of auxiliary weights to allow of its use with spirits of widely varying strengths. [Translator.]

<div align="center">TABLE XXV</div>

Table for the Dilution of 100 c.c. of Alcohol of 100–90.1% by Volume to bring it to 90% by Volume

Concentration of Alcohol.	Water to be added (c.c.).	Concentration of Alcohol.	Water to be added (c.c.).	Concentration of Alcohol.	Water to be added (c.c.)	Concentration of Alcohol.	Water to be added (c.c.).
100	13·2	97·5	9·7	95	6·4	92·5	3·1
99·9	13·1	97·4	9·5	94·9	6·3	92·4	3
99·8	12·9	97·3	9·4	94·8	6·1	92·3	2·9
99·7	12·8	97·2	9·2	94·7	6	92·2	2·7
99·6	12·6	97·1	9·1	94·6	5·9	92·1	2·6
99·5	12·5	97	9	94·5	5·7	92	2·5
99·4	12·3	96·9	8·9	94·4	5·6	91·9	2·4
99·3	12·2	96·8	8·7	94·3	5·5	91·8	2·2
99·2	12	96·7	8·6	94·2	5·3	91·7	2·1
99·1	11·9	96·6	8·5	94·1	5·2	91·6	2
99	11·8	96·5	8·3	94	5·1	91·5	1·8
98·9	11·7	96·4	8·2	93·9	5	91·4	1·7
98·8	11·5	96·3	8·1	93·8	4·8	91·3	1·6
98·7	11·4	96·2	7·9	93·7	4·7	91·2	1·4
98·6	11·3	96·1	7·8	93·6	4·6	91·1	1·3
98·5	11·1	96	7·7	93·5	4·4	91	1·2
98·4	10·9	95·9	7·6	93·4	4·3	90·9	1·1
98·3	10·8	95·8	7·4	93·3	4·2	90·8	0·9
98·2	10·6	95·7	7·3	93·2	4	90·7	0·8
98·1	10·5	95·6	7·2	93·1	3·9	90·6	0·7
98	10·4	95·5	7	93	3·8	90·5	0·5
97·9	10·3	95·4	6·9	92·9	3·7	90·4	0·4
97·8	10·1	95·3	6·8	92·8	3·5	90·3	0·3
97·7	10	95·2	6·6	92·7	3·4	90·2	0·2
97·6	9·8	95·1	6·5	92·6	3·3	90·1	0·1

3. Determination of the Extract and Ash

As a rule spirits do not contain an appreciable proportion of fixed matter, so that determinations of the extract and ash are scarcely ever necessary with spirits ; they should, however, be carried out with liqueurs, the procedure being as with wines (q.v.).

4. Detection and Determination of Impurities

The principal impurities which may occur naturally in an alcohol are acids, esters, furfuraldehyde and other aldehydes and higher alcohols. They are determined by the methods given below in the liquid distilled and prepared as described.

With liqueurs it is further necessary, before investigating the volatile impurities, to eliminate any essential oils present, but it must be remembered that in such case the results obtained are not perfectly certain,

The impurities are expressed in milligrams per 100 c.c. of anhydrous alcohol contained in the spirit. The sum of the different impurities, also referred to 100 c.c. of anhydrous alcohol, represents the so-called *coefficient of impurity*.

1. Preparation of the Liquid to be examined.—Some of the determinations require that the alcohol should be brought exactly to the strength of 50% (by volume). Two cases present themselves :

(A) *The alcohol to be examined is weaker than* 50%.

In such case it is necessary to add a suitable quantity of a stronger alcohol. For this purpose use is made of 90% alcohol, which, in its turn, is obtained from a more concentrated alcohol by addition of the proportion of water given in Table XXV, (p. 238).

For instance, 8·1 c.c. of water must be added to 100 c.c. of 96·3% (by volume) alcohol to obtain a mixture of 90% (by volume) concentration.

When the 90% alcohol is obtained, the amount of this to be added to 100 c.c. of any alcohol having a strength between 30% and 49·9% to bring it to the concentration 50% is given in Table XXVI ; column I gives the concentration of the alcohol to be strengthened, column II the number of c.c. of 90% alcohol to be added to 100 c.c., and column III the volume of the mixture obtained.[1]

Thus, with a distilled alcohol of 47·2% (by volume) concentration, 100 c.c. must be mixed with 6·8 c.c. of 90% alcohol to give 106·6 c.c. of 50% alcohol.[2]

(B) *The alcohol to be examined is stronger than* 50%.

In this case water must be added and the amount necessary is shown in Fig. XXVII ; column II gives the number of c.c. of water [3] to be added to 100 c.c. of an alcohol of the concentration shown in column I and column III the volume of the mixture thus obtained.[4]

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[1] These quantities are deduced from the general formula :

$$x = 100 \frac{a\,P - A\,p}{A\,p' - a'\,P},$$

which serves for the calculation of the quantity x of pure alcohol of strength a' and specific gravity p' (at 15°) to be added to 100 c.c. of alcohol of strength a and specific gravity p to bring it to the strength A corresponding with the specific gravity P.

[2] This volume is calculated from the general formula, $V = (100\,a + x\,a') \div A$, where a, a' and A have the same significance as in the previous note.

[3] These volumes are calculated from the general formula, $x = 100\,(a\,P - A\,p) \div A$, which serves for the calculation of the quantity of water x to be added to 100 c.c. of alcohol of strength a and specific gravity p to bring it to the lower strength A corresponding with the specific gravity P.

[4] This volume is calculated from the general formula, $V = 100\,a \div A$, where a and A have the same significations as in the previous note.

TABLE XXVI

Number of c.c. of 90% Alcohol to be added to 100 c.c. of 30–49.9% Alcohol to bring the Concentration to 50%

Concentration of the Alcohol. I	C.c. of 90% Alcohol required. II	Volume of Mixture in c.c. III
30	47·7	145·9
·1	47·5	145·7
·2	47·3	145·5
·3	47·1	145·3
·4	46·8	145
·5	46·6	144·8
·6	46·4	144·6
·7	46·2	144·4
·8	45·9	144·2
·9	45·6	143·9
31	45·4	143·7
·1	45·2	143·5
·2	45	143·3
·3	44·7	143
·4	44·5	142·8
·5	44·3	142·6
·6	44	142·3
·7	43·8	142·1
·8	43·6	141·9
·9	43·4	141·7
32	43·1	141·5
·1	42·9	141·2
·2	42·7	141
·3	42·5	140·8
·4	42·2	140·6
·5	42	140·4
·6	41·7	140·2
·7	41·5	140
·8	41·2	139·8
·9	40·9	139·5
33	40·7	139·3
·1	40·5	139·1
·2	40·2	138·8
·3	40	138·6
·4	39·8	138·4
·5	39·6	138·1
·6	39·3	137·9
·7	39·1	137·7
·8	38·9	137·5
·9	38·7	137·3
34	38·4	137
·1	38·1	136·8
·2	37·9	136·6
·3	37·7	136·4
·4	37·5	136·2
·5	37·2	135·9
·6	37	135·7
·7	36·7	135·5
·8	36·5	135·3
·9	36·3	135·1
35	36	134·8
·1	35·7	134·5
·2	35·5	134·3
·3	35·3	134·1
·4	35	133·8
·5	34·8	133·6
·6	34·6	133·4
·7	34·3	133·2
·8	34	132·9
·9	33·8	132·7
36	33·6	132·5
·1	33·4	132·3
·2	33·1	132
·3	32·9	131·8
·4	32·7	131·6
·5	32·4	131·4
·6	32·2	131·2
·7	32	131
·8	31·7	130·7
·9	31·5	130·5
37	31·3	130·3
·1	31	130
·2	30·7	129·8
·3	30·5	129·6
·4	30·3	129·4
·5	30	129·1
·6	29·8	128·9
·7	29·5	128·6
·8	29·3	128·4
·9	29·1	128·2
38	28·9	128
·1	28·7	127·8
·2	28·5	127·6
·3	28·3	127·4
·4	28	127·1
·5	27·8	126·9
·6	27·5	126·6
·7	27·2	126·3
·8	27	126·1
·9	26·8	125·9
39	26·5	125·6
·1	26·3	125·4
·2	26·1	125·2
·3	25·8	124·9
·4	25·6	124·7
·5	25·3	124·5
·6	25·1	124·3
·7	24·8	124
·8	24·6	123·8
·9	24·3	123·5
40	24·1	123·3
·1	23·9	123·1
·2	23·7	122·9
·3	23·5	122·7
·4	23·3	122·5
·5	23	122·3
·6	22·8	122·1
·7	22·5	121·8
·8	22·2	121·5
·9	22	121·3
41	21·8	121·1
·1	21·5	120·8
·2	21·3	120·6
·3	21	120·3
·4	20·7	120·1
·5	20·5	119·9
·6	20·3	119·7
·7	20	119·4
·8	19·8	119·2
·9	19·5	118·9
42	19·3	118·7
·1	19	118·4
·2	18·7	118·2
·3	18·5	118
·4	18·3	117·8
·5	18·1	117·6
·6	17·9	117·4
·7	17·7	117·2
·8	17·4	116·9
·9	17·2	116·7
43	16·9	116·4
·1	16·7	116·2
·2	16·5	116
·3	16·2	115·7
·4	15·9	115·5
·5	15·7	115·2
·6	15·5	115
·7	15·2	114·7
·8	14·9	114·5
·9	14·7	114·3
44	14·5	114·1
·1	14·2	113·8
·2	13·9	113·5
·3	13·7	113·3
·4	13·5	113·1
·5	13·3	112·9
·6	13·1	112·7
·7	12·8	112·4
·8	12·6	112·2
·9	12·4	112
45	12·1	111·8
·1	11·9	111·6
·2	11·7	111·4
·3	11·4	111·1
·4	11·1	110·8
·5	10·9	110·6
·6	10·7	110·4
·7	10·4	110·1
·8	10·1	109·8
·9	9·9	109·6
46	9·7	109·4
·1	9·4	109·1
·2	9·1	108·8
·3	8·9	108·6
·4	8·7	108·4
·5	8·5	108·2
·6	8·2	107·9
·7	7·9	107·7
·8	7·7	107·5
·9	7·5	107·3
47	7·3	107·1
·1	7·1	106·9
·2	6·8	106·6
·3	6·6	106·4
·4	6·4	106·2
·5	6·1	105·9
·6	5·9	105·7
·7	5·7	105·5
·8	5·4	105·2
·9		104·9
48	4·9	104·7
·1	4·6	104·4
·2	4·4	104·2
·3	4·1	103·9
·4	3·9	103·7
·5	3·6	103·5
·6	3·3	103·2
·7	3·1	103
·8	2·8	102·7
·9	2·6	102·5
49	2·4	102·3
·1	2·1	102
·2	1·9	101·8
·3	1·7	101·6
·4	1·5	101·4
·5	1·2	101·2
·6	·9	100·9
·7	·7	100·7
·8	·4	100·4
·9	·2	100·2

TABLE XXVII

Number of c.c. of Water to be added to 100 c.c. of 50·1–100% Alcohol to give a Mixture of 50% Concentration

Strength of the Alcohol.	C.c. of Water required.	Volume of the Mixture.	Strength of the Alcohol.	C.c. of Water required.	Volume of the Mixture.	Strength of the Alcohol.	C.c. of Water required.	Volume of the Mixture.	Strength of the Alcohol.	C.c.of Water required.	Volume of the Mixture.	Strength of the Alcohol.	C.c. of Water required.	Volume of the Mixture.
I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
50·1	0·21	100·19	55·1	10·37	110·1	60·1	20·97	120·1	65·1	31·44	130·1	70·1	41·99	140·1
50·2	0·41	100·38	55·2	10·78	110·3	60·2	21·18	120·3	65·2	31·63	130·3	70·2	42·20	140·3
50·3	0·62	100·57	55·3	10·98	110·5	60·3	21·39	120·5	65·3	31·86	130·5	70·3	42·41	140·5
50·4	0·82	100·76	55·4	11·19	110·7	60·4	21·60	120·7	65·4	32·07	130·7	70·4	42·62	140·7
50·5	1·03	100·95	55·5	11·40	110·9	60·5	21·80	120·9	65·5	32·28	130·9	70·5	42·83	140·9|
50·6	1·24	101·14	55·6	11·61	111·1	60·6	22·01	121·1	65·6	32·49	131·1	70·6	43·05	141·1
50·7	1·44	101·33	55·7	11·81	111·3	60·7	22·22	121·3	65·7	32·70	131·3	70·7	43·26	141·3
50·8	1·65	101·52	55·8	12·02	111·5	60·8	22·43	121·5	65·8	32·91	131·5	70·8	43·47	141·5
50·9	1·85	101·71	55·9	12·23	111·7	60·9	22·64	121·7	65·9	33·12	131·7	70·9	43·68	141·7
51	2·06	101·9	56	12·44	111·9	61	22·85	121·9	66	33·33	131·9	71	43·89	141·9
51·1	2·27	102·1	56·1	12·65	112·1	61·1	23·06	122·1	66·1	33·54	132·1	71·1	44·10	142·1
51·2	2·47	102·3	56·2	12·85	112·3	61·2	23·27	122·3	66·2	33·75	132·3	71·2	44·31	142·3
51·3	2·68	102·5	56·3	13·06	112·5	61·3	23·48	122·5	66·3	33·96	132·5	71·3	44·52	142·5
51·4	2·89	102·7	56·4	13·27	112·7	61·4	23·69	122·7	66·4	34·17	132·7	71·4	44·73	142·7
51·5	3·09	102·9	56·5	13·48	112·9	61·5	23·90	122·9	66·5	34·38	132·9	71·5	44·94	142·9
51·6	3·30	103·1	56·6	13·69	113·1	61·6	24·11	123·1	66·6	34·60	133·1	71·6	45·16	143·1
51·7	3·51	103·3	56·7	13·90	113·3	61·7	24·32	123·3	66·7	34·81	133·3	71·7	45·37	143·3
51·8	3·72	103·5	56·8	14·10	113·5	61·8	24·53	123·5	66·8	35·02	133·5	71·8	45·58	143·5
51·9	3·92	103·7	56·9	14·31	113·7	61·9	24·74	123·7	66·9	35·23	133·7	71·9	45·79	143·7
52	4·13	103·9	57	14·52	113·9	62	24·95	123·9	67	35·44	133·9	72	46	143·9
52·1	4·34	104·1	57·1	14·73	114·1	62·1	25·16	124·1	67·1	35·65	134·1	72·1	46·21	144·1
52·2	4·54	104·3	57·2	14·94	114·3	62·2	25·37	124·3	67·2	35·86	134·3	72·2	46·43	144·3
52·3	4·75	104·5	57·3	15·14	114·5	62·3	25·58	124·5	67·3	36·07	134·5	72·3	46·64	144·5
52·4	4·96	104·7	57·4	15·35	114·7	62·4	25·79	124·7	67·4	36·28	134·7	72·4	46·85	144·7
52·5	5·16	104·9	57·5	15·56	114·9	62·5	25·99	124·9	67·5	36·49	134·9	72·5	47·06	144·9
52·6	5·37	105·1	57·6	15·77	115·1	62·6	26·20	125·1	67·6	36·71	135·1	72·6	47·28	145·1
52·7	5·58	105·3	57·7	15·98	115·3	62·7	26·41	125·3	67·7	36·92	135·3	72·7	47·49	145·3
52·8	5·79	105·5	57·8	16·18	115·5	62·8	26·62	125·5	67·8	37·13	135·5	72·8	47·70	145·5
52·9	5·99	105·7	57·9	16·39	115·7	62·9	26·83	125·7	67·9	37·34	135·7	72·9	47·92	145·7
53	6·20	105·9	58	16·60	115·9	63	27·04	125·9	68	37·55	135·9	73	48·13	145·9
53·1	6·41	106·1	58·1	16·81	116·1	63·1	27·25	126·1	68·1	37·76	136·1	73·1	48·34	146·1
53·2	6·62	106·3	58·2	17·02	116·3	63·2	27·46	126·3	68·2	37·97	139·3	73·2	48·55	146·3
53·3	6·82	106·5	58·3	17·22	116·5	63·3	27·67	126·5	68·3	38·18	136·5	73·3	48·77	146·5
53·4	7·03	106·7	58·4	17·43	116·7	63·4	27·88	126·7	68·4	38·39	136·7	73·4	48·98	146·7
53·5	7·24	106·9	58·5	17·64	116·9	63·5	28·09	126·9	68·5	38·60	136·9	73·5	49·19	146·9
53·6	7·45	107·1	58·6	17·85	117·1	63·6	28·30	127·1	68·6	38·82	137·1	73·6	49·40	147·1
53·7	7·66	107·3	58·7	18·06	117·3	63·7	28·51	127·3	68·7	39·03	137·3	73·7	49·61	147·3
53·8	7·86	107·5	58·8	18·26	117·5	63·8	28·72	127·5	68·8	39·24	137·5	73·8	49·83	147·5
53·9	8·07	107·7	58·9	18·47	117·7	63·9	28·93	127·7	68·9	39·45	137·7	73·9	50·04	147·7
54	8·28	107·9	59	18·68	117·9	64	29·14	127·9	69	39·66	137·9	74	50·25	147·9
54·1	8·49	108·1	59·1	18·89	118·1	64·1	29·35	128·1	69·1	39·87	138·1	74·1	50·46	148·1
54·2	8·70	108·3	59·2	19·10	118·3	64·2	29·56	128·3	69·2	40·08	138·3	74·2	50·68	148·3
54·3	8·90	108·5	59·3	19·30	118·5	64·3	29·77	128·5	69·3	40·30	138·5	74·3	50·89	148·5
54·4	9·11	108·7	59·4	19·51	118·7	64·4	29·98	128·7	69·4	40·51	138·7	74·4	51·10	148·7
54·5	9·32	108·9	59·5	19·72	118·9	64·5	30·18	128·9	69·5	40·72	138·9	74·5	51·31	148·9
54·6	9·53	109·1	59·6	19·93	119·1	64·6	30·39	129·1	69·6	40·93	139·1	74·6	51·53	149·1
54·7	9·74	109·3	59·7	20·14	119·3	64·7	30·60	129·3	69·7	41·14	139·3	74·7	51·74	149·3
54·8	9·94	109·5	59·8	20·34	119·5	64·8	30·81	129·5	69·8	41·36	139·5	74·8	51·95	149·5
54·9	10·13	109·7	59·9	20·55	119·7	64·9	31·02	129·7	69·9	41·57	139·7	74·9	52·17	149·7
55	10·37	109·9	60	20·76	119·9	65	31·23	129·9	70	41·78	139·9	75	52·38	149·9

TABLE XXVII—*continued*

Strength of the Alcohol.	C.c. of Water required.	Volume of the Mixture.	Strength of the Alcohol.	C.c. of Water required.	Volume of the Mixture.	Strength of the Alcohol.	C.c. of Water required.	Volume of the Mixture.	Strength of the Alcohol.	C.c. of Water required.	Volume of the Mixture.	Strength of the Alcohol.	C.c. of Water required.	Volume of the Mixture.
I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
75·1	52·59	150·1	80·1	63·28	160·1	85·1	74·07	170·1	90·1	84·98	180·1	95·1	96·10	190·1
75·2	52·81	150·3	80·2	63·50	160·3	85·2	74·28	170·3	90·2	85·20	180·3	95·2	96·32	190·3
75·3	53·02	150·5	80·3	63·71	160·5	85·3	74·50	170·5	90·3	85·42	180·5	95·3	96·55	190·5
75·4	53·23	150·7	80·4	63·93	160·7	85·4	74·72	170·7	90·4	85·64	180·7	95·4	96·78	190·7
75·5	53·44	150·9	80·5	64·14	160·9	85·5	74·93	170·9	90·5	85·86	180·9	95·5	97	190·9
75·6	53·66	151·1	80·6	64·36	161·1	85·6	75·15	171·1	90·6	86·08	181·1	95·6	97·23	191·1
75·7	53·87	151·3	80·7	64·57	161·3	85·7	75·37	171·3	90·7	86·30	181·3	95·7	97·46	191·3
75·8	54·08	151·5	80·8	64·79	161·5	85·8	75·57	171·5	90·8	86·52	181·5	95·8	97·69	191·5
75·9	54·30	151·7	80·9	65	161·7	85·9	75·80	171·7	90·9	86·74	181·7	95·9	97·91	191·7
76	54·51	151·9	81	65·22	161·9	86	76·02	171·9	91	86·96	181·9	96	98·14	191·9
76·1	54·72	152·1	81·1	65·43	162·1	86·1	76·24	172·1	91·1	87·18	182·1	96·1	98·37	192·1
76·2	54·94	152·3	81·2	65·65	162·3	86·2	76·45	172·3	91·2	87·40	182·3	96·2	98·60	192·3
76·3	55·15	152·5	81·3	65·86	162·5	86·3	76·67	172·5	91·3	87·63	182·5	96·3	98·83	192·5
76·4	55·37	152·7	81·4	66·08	162·7	86·4	76·89	172·7	91·4	87·85	182·7	96·4	99·06	192·7
76·5	55·58	152·9	81·5	66·29	162·9	86·5	77·10	172·9	91·5	88·07	182·9	96·5	99·28	192·9
76·6	55·79	153·1	81·6	66·51	163·1	86·6	77·32	173·1	91·6	88·29	183·1	96·6	99·51	193·1
76·7	56·01	153·3	81·7	66·72	163·3	86·7	77·54	173·3	91·7	88·51	183·3	96·7	99·74	193·3
76·8	56·22	153·5	81·8	66·94	163·5	86·8	77·76	173·5	91·8	88·74	183·5	96·8	99·97	193·5
76·9	56·44	153·7	81·9	67·15	163·7	86·9	77·97	173·7	91·9	88·96	183·7	96·9	100·20	193·7
77	56·65	153·9	82	67·37	163·9	87	78·19	173·9	92	89·18	183·9	97	100·43	193·9
77·1	56·86	154·1	82·1	67·59	164·1	87·1	78·41	174·1	92·1	89·40	184·1	97·1	100·66	194·1
77·2	57·08	154·3	82·2	67·80	164·3	87·2	78·63	174·3	92·2	89·62	184·3	97·2	100·89	194·3
77·3	57·29	154·5	82·3	68·01	164·5	87·3	78·84	174·5	92·3	89·85	184·5	97·3	101·12	194·5
77·4	57·51	154·7	82·4	68·23	164·7	87·4	79·06	174·7	92·4	90·07	184·7	97·4	101·35	194·7
77·5	57·72	154·9	82·5	68·45	164·9	87·5	79·28	174·9	92·5	90·29	184·9	97·5	101·58	194·9
77·6	57·94	155·1	82·6	68·67	165·1	87·6	79·50	175·1	92·6	90·51	185·1	97·6	101·81	195·1
77·7	58·15	155·3	82·7	68·88	165·3	87·7	79·72	175·3	92·7	90·73	185·3	97·7	102·04	195·3
77·8	58·36	155·5	82·8	69·10	165·5	87·8	79·93	175·5	92·8	90·96	185·5	97·8	102·27	195·5
77·9	58·57	155·7	82·9	69·31	165·7	87·9	80·15	175·7	92·9	91·18	185·7	97·9	102·50	195·7
78	58·79	155·9	83	69·53	165·9	88	80·37	175·9	93	91·40	185·9	98	102·73	195·9
78·1	59	156·1	83·1	69·75	166·1	88·1	80·59	176·1	93·1	91·62	186·1	98·1	102·96	196·1
78·2	59·22	156·3	83·2	69·96	166·3	88·2	80·81	176·3	93·2	91·84	186·3	98·2	103·20	196·3
78·3	59·43	156·5	83·3	70·18	166·5	88·3	81·03	176·5	93·3	92·07	186·5	98·3	103·43	196·5
78·4	59·65	156·7	83·4	70·39	166·7	88·4	81·25	176·7	93·4	92·29	186·7	98·4	103·66	196·7
78·5	59·86	156·9	83·5	70·61	166·9	88·5	81·46	176·9	93·5	92·51	186·9	98·5	103·89	196·9
78·6	60·07	157·1	83·6	70·83	167·1	88·6	81·68	177·1	93·6	92·73	187·1	98·6	104·13	197·1
78·7	60·29	157·3	83·7	71·04	167·3	88·7	81·90	177·3	93·7	92·95	187·3	98·7	104·36	197·3
78·8	60·50	157·5	83·8	71·26	167·5	88·8	82·12	177·5	93·8	93·18	187·5	98·8	104·59	197·5
78·9	60·72	157·7	83·9	71·47	167·7	88·9	82·34	177·7	93·9	93·40	187·7	98·9	104·83	197·7
79	60·93	157·9	84	71·69	167·9	89	82·56	177·9	94	93·62	187·9	99	105·06	197·9
79·1	61·14	158·1	84·1	71·91	168·1	89·1	82·78	178·1	94·1	93·84	188·1	99·1	105·30	198·1
79·2	61·36	158·3	84·2	72·12	168·3	89·2	83	178·3	94·2	94·07	188·3	99·2	105·54	198·3
79·3	61·57	158·5	84·3	72·34	168·5	89·3	83·22	178·5	94·3	94·29	188·5	99·3	105·77	198·5
79·4	61·79	158·7	84·4	72·55	168·7	89·4	83·44	178·7	94·4	94·52	188·7	99·4	106·01	198·7
79·5	62	158·9	84·5	72·77	168·9	89·5	83·66	178·9	94·5	94·74	188·9	99·5	106·25	198·9
79·6	62·21	159·1	84·6	72·99	169·1	89·6	83·88	179·1	94·6	94·97	189·1	99·6	106·49	199·1
79·7	62·43	159·3	84·7	73·20	169·3	89·7	84·10	179·3	94·7	95·19	189·3	99·7	106·73	199·3
79·8	62·64	159·5	84·8	73·42	169·5	89·8	84·32	179·5	94·8	95·43	189·5	99·8	106·96	199·5
79·9	62·86	159·7	84·9	73·63	169·7	89·9	84·54	179·7	94·9	95·64	189·7	99·9	107·20	199·7
80	63·07	159·9	85	73·85	169·9	90	84·76	179·9	95	95·87	189·9	100	107·44	199·9

Thus, 52.8 c.c. of water must be added to 100 c.c. of 75% alcohol to give 149% c.c. of 50% alcohol.

2. Determination of the Acidity. The acids naturally occurring in a spirit are mainly acetic acid, together with butyric, formic, propionic, valeric, caproic, oenanthic, caprylic, pelargonic, caprinic, palmitic, etc. As a rule these are determined together in the following manner : 50 c.c. of the liquid are titrated with N/10 KOH in presence of phenolphthalein if the liquid is almost colourless, or with the help of moistened sensitive violet litmus paper (azolitmin paper), if the liquid is appreciably coloured. Some spirits contain dissolved carbon dioxide, which may be detected by means of lime-water and should be expelled by boiling the liquid in a reflux apparatus before determining the acids.

EXAMPLE.—50 c.c. of a sample of spirits of 92% strength require 5 c.c. of N/10 KOH for neutralisation. The acidity in milligrams of acetic acid per 100 c.c. of the spirit will be, ... or, with reference to 100 c.c. of anhydrous spirit, 60 × 100 ÷ 92 = 65 mgrms.

If fixed acids are present, these may be determined separately by titration of the residue left by 25 c.c. of liquid evaporated in a vacuum desiccator ; volatile acidity = total acidity - fixed acidity. Some products, for instance, kirschwasser, contain hydrocyanic acid, which is readily detected by the odour and is determined as indicated later.

In some cases sulphuric, hydrochloric and sulphurous acids may be present. The first two are detected by the ordinary analytical methods or by the procedure given for vinegar (see Vol. II, Chapter VI, Paragraphs 6 and 7). Sulphurous acid is readily recognised and may be determined by iodometric titration.

3. Determination of the Esters. The esters naturally present in spirits are the ethyl and homologous esters of the fatty acids mentioned above, ethyl acetate being the principal one. Other esters in larger quantities may be found in certain liqueurs and spirits which are artificially perfumed. The esters are determined together in the distilled spirit in the following manner.

50 c.c. of the alcoholic liquid, neutralised for the determination of the acidity, are boiled for an hour in a reflux apparatus with 20 c.c. of decinormal alkali hydroxide. When cold, the liquid is treated with 20 c.c. of N/10 H_2SO_4 and the excess of acid titrated with N/10 KOH. The number of c.c. of potash used for such titration will correspond with the alkali used for the saponification of the esters in 50 c.c. of the liquid. c.c. of N/10-KOH × 8.81 = milligrams of ethyl acetate.[1] Twice this product is the quantity of esters in 100 c.c. of the spirit and if this is multiplied by 100 and the result divided by the alcoholic strength of the spirit, the value referred to 100 parts of absolute alcohol is obtained.

EXAMPLE.—Saponification of 50 c.c. of a 45% (by vol.) spirit required 12.5 c.c. of N/10 KOH. 100 c.c. of this spirit thus contain 12.5 × 8.81 × 2 = 220 mgrms. of ethyl acetate, while the amount of the spirit corresponding with 100 c.c. of absolute alcohol contains 220 × 100 ÷ 45 = 488 mgrms. of ethyl acetate.

[1] By some the results are expressed simply as the number of c.c. of N/10-potash used to hydrolyse the esters present in 100 c.c. of the liquid (*Ester index*).

4. Detection and Determination of the Aldehydes.—The aldehydes present in spirits are mainly acetaldehyde, paraldehyde, formaldehyde, acetal and, in small quantities, higher homologous aldehydes (butyraldehyde, valeraldehyde) and other aldehydes (acraldehyde, furfuraldehyde, etc.). They are detected and determined as follows :

(*A*) DETECTION. This is effected by one of the following tests :

1. *With potash* (Liebig). A mixture of equal volumes of the alcohol to be tested and 20% potassium hydroxide solution is gradually heated in a test-tube to boiling. Pure alcohol is scarcely coloured, whereas in presence of smaller or larger amounts of aldehydes, a yellow or reddish brown coloration is formed.

2. *Schiff's reaction.* 10 c.c. of the alcohol (50%) and 4 c.c. of Schiff's reagent (*see* below : Determination) are shaken together in a test-tube and allowed to stand. The presence of aldehydes is shown by the appearance, either immediately or after some time, of a more or less intense red coloration, which should be observed after about 20 minutes. If no colour appears after this time, the liquid is free from aldehydes.

As this reaction is extremely sensitive and a faint coloration may be given by other substances than aldehydes, a very slight pink colour cannot be regarded as a certain sign of the presence of aldehydes.

3. *Metaphenylenediamine reaction* (Windisch). To 10 c.c. of the spirit in a porcelain dish is added, drop by drop, 1 c.c. of fresh 10% metaphenylenediamine hydrochloride solution, mixing of the two liquids being avoided. In presence of small amounts of aldehydes, after 2–4 minutes there forms at the surface of contact of the two liquids a more or less intense yellow or orange-red coloration, while later there appears a green fluorescence, which is shown more especially on heating.

This reaction is very sensitive, although less so than the preceding, but it does not lend itself to colorimetric determination.

(*B*) QUANTITATIVE DETERMINATION. This is carried out with the help of Schiff's reagent, comparison being made with a standard solution.

Reagents : 1. Schiff's reagent. To a litre of distilled water are added 150 c.c. of fresh 0·1% aqueous fuchsine (not sulphonate) solution and then 100 c.c. of sodium bisulphite solution of sp. gr. 1·36 and, after mixing, 15 c.c. of pure concentrated sulphuric acid. After some hours the mixture should be clear and colourless ; it should be kept in the dark in well-stoppered bottles and should not be used until some days old.

2. Pure alcohol. Pure alcohol of commerce of at least 96% strength is neutralised exactly, boiled for an hour in a reflux apparatus with 1–2% of metaphenylenediamine hydrochloride and then distilled, the first and last portions of the distillate being discarded. The sp. gr. of the alcohol thus obtained is determined and the strength adjusted to 90% or 50% (*see* Tables XXV and XXVII). This alcohol should not colour either with Schiff's reagent or when heated for an hour with an equal volume of concentrated sulphuric acid in a bath at 120°.

3. Standard solution. 0·1387 gram of aldehyde-ammonia (freshly prepared, washed with anhydrous ether and dried over sulphuric acid), corresponding with 0·1 gram of acetaldehyde, is dissolved in a 100 c.c. flask in

about 50 c.c. of 50% alcohol free from aldehydes. The solution is then treated with 2·27 c.c. of N-sulphuric acid and 2·5 c.c. of pure 90% alcohol (so that the strength is not altered by the water of the normal sulphuric acid) and the whole made up to 100 c.c. with pure 50% alcohol. The liquid is mixed and filtered, and exactly 50 c.c. of the filtrate diluted to a litre with pure 50% alcohol. The solution then contains 0·05 gram of acetaldehyde per litre.

Procedure. 10 c.c. of the spirits, brought to 50% strength, are placed in one test-tube and 10 c.c. of the standard solution in another, 4 c.c. of Schiff's reagent being added in each case and the tubes then closed, shaken and left for 20 minutes. If the two liquids then have about equally intense colorations, they are compared in the colorimeter. Otherwise the test is repeated, a less quantity being taken of the alcohol giving the deeper coloration and this made up to 10 c.c. with pure 50% alcohol ; this is necessary because the intensities of the coloration are not proportional to the aldehyde-content, except when the differences are small. When sensibly similar colorations are obtained, the liquids are compared in the Duboscq colorimeter.

Calculation of the results. Suppose c c.c. of the spirits to be examined (50%) are made up to 10 c.c. with pure 50% alcohol. If in the colorimeter m millimetres of this liquid correspond with m' millimetres of the standard aldehyde solution, 100 c.c. of the 50% spirits will contain $(5 \times 10 \times m') \div (c \times m)$ milligrams of aldehyde. If, on the other hand, the colorimetric test requires dilution of the standard solution (c' c.c. being made up to 10 c.c.), the result is given by $(5 \times c' \times m') \div (10 \times m)$. The result must be corrected for the dilution or concentration of the original spirit **to** bring it to 50% strength and is then calculated so as to correspond with 100 c.c. of anhydrous alcohol.

EXAMPLES : (1) 100 c.c. of 45% spirits are mixed with 12·1 c.c. of pure 90% alcohol to give 111·8 c.c. of 50% strength. After dilution of 5 c.c. of this spirit to 10 c.c. with pure 50% alcohol, and treatment with Schiff's reagent, a column 12 mm. deep was found to correspond with a column of the standard aldehyde solution 10 mm. deep. 100 c.c. of the spirit diluted to 50% thus contain

$$5 \times \frac{10}{5} \times \frac{10}{12} = 8·3 \text{ mgrms. of aldehyde.}$$

100 c.c. of the original 45% spirit contain

$$\frac{8·3 \times 111·8}{100} = 9·28 \text{ mgrms. of aldehyde,}$$

and the amount of aldehyde referred to 100 c.c. of anhydrous alcohol will be

$$\frac{8·3 \times 111·8}{45} = 20·6 \text{ mgrms.}$$

(2) With another sample of 45% spirit, it was necessary to dilute 5 c.c. of the standard aldehyde solution to 10 c.c., 9 mm. of this liquid then corresponding with 10 mm. of the spirit under investigation (duly brought to 50% strength). Thus, 100 c.c. of the spirits (50%) contain

$$5 \times \frac{5}{10} \times \frac{9}{10} = 2·25 \text{ mgrms. of aldehyde,}$$

100 c.c. of the original 45% spirits:

$$\frac{2 \cdot 25 \times 111 \cdot 8}{100} = 2 \cdot 50 \text{ mgrms.,}$$

and 100 c.c. of anhydrous alcohol

$$\frac{2 \cdot 25 \times 111 \cdot 8}{45} = 5 \cdot 25 \text{ mgrms. of aldehyde.}$$

5. Detection and Determination of Furfural.—(*A*) QUALITATIVE TEST. 10 c.c. of the spirits are shaken with 10 drops of aniline and 1 c.c. of concentrated acetic acid and then allowed to stand : in presence of furfural, a red coloration forms either immediately or after some time.

This reaction is extremely sensitive ; freshly distilled pure aniline should be used and the acetic acid should be pure and should not give the furfural reaction. Spirits which have been stored in wooden casks give with aniline acetate a yellow coloration which disturbs the reaction ; in such cases the spirit should be distilled before testing.

(*B*) QUANTITATIVE DETERMINATION. The above reaction may be utilised for a colorimetric determination.

For this purpose a *standard solution* containing 0·005 gram of furfural per litre of pure 50% alcohol is prepared, the spirit to be tested being also brought to 50% concentration. 10 c.c. of each of the two liquids are treated at the same time with 10 drops of aniline and 1 c.c. of concentrated acetic acid. If, after 20 minutes, the colorations are approximately similar, they are compared in the Duboscq colorimeter ; if, however, the two colorations differ greatly, the test is repeated in the manner described for the determination of the aldehydes (*see* above). The proportion of furfuraldehyde present is readily calculated from the colorimeter readings.

6. Determination of the Higher Alcohols.—The higher alcohols found in spirits are the products of secondary fermentations and consist principally of amyl alcohol, together with isobutyl, butyl, propyl and, in small amounts, higher homologous alcohols.

Their presence in marked quantity is *detected* by the turbidity appearing on dilution of the spirit with water and by the amylic odour observed when a little of the spirit is rubbed between the hands.

For the *quantitative* determination of these impurities, the following two methods are available, the first being preferable with potable spirits and liqueurs and the second with industrial spirit.

1. COLORIMETRIC METHOD (Rocques). This is based on the brown coloration given by alcohols (especially those with non-normal chains) when heated with concentrated sulphuric acid. It should be carried out on the alcohols brought to a definite strength and freed from aldehydes, which also give an intense brown coloration with sulphuric acid. The determination is made colorimetrically, by comparison with a suitable standard solution.

Standard solution. This is prepared from isobutyl alcohol, which, of the higher alcohols, is that giving the deepest coloration with sulphuric acid ; the higher alcohol predominating in spirits is, however, amyl alcohol. Naturally the results obtained are conventional, but are always comparable one with the other.

The isobutyl alcohol to be used should be prepared as follows : The isobutyl alcohol of commerce is subjected to three successive distillations. In the first of these the fraction passing over at 106·5–107·5° is collected and again distilled slowly through rectification bulbs, the fraction distilling at 106·7–107·1° being distilled a third time, when the portion boiling at 106·8–107° is collected ; this is the fraction employed. Pure ethyl alcohol, which gives no reaction with sulphuric acid (see p. 244), is also prepared and made up to 66·7% (by volume) strength [1] ; with this a solution containing 0·667 gram of isobutyl alcohol per litre is prepared.

Preliminary preparation of the alcoholic liquid. The spirit must be freed from aldehydes and made up to a definite strength. To this end, 100 c.c. of the spirit, made up to 50% strength (see p. 245), are placed in a flask of about 250 c.c. capacity together with 2 grams of metaphenylenediamine hydrochloride and a few pieces of pumice, the liquid being then boiled fairly gently under a reflux condenser for an hour. After cooling, the liquid is distilled, exactly 75 c.c. of distillate being collected in a flask of that capacity. The liquid thus collected contains all the alcohol existing in the 100 c.c. of spirit and will contain, therefore, 66·7% of alcohol (by volume) ; this is used for the reaction.

Procedure. Into a perfectly clean, dry flask of capacity about 100 c.c. and with a neck about 20 cm. long, are poured 10 c.c. of the spirit to be examined (prepared as described above) and, by means of a pipette, 10 c.c. of pure concentrated sulphuric acid, which is allowed to flow down the side of the flask so that it does not mix with the alcoholic liquid ; the flask is at once vigorously shaken and placed in a bath at 120°. This bath may contain a 69% calcium chloride solution ; the level and concentration are kept constant by means of an inverted flask full of water and closed by a stopper traversed by a large glass tube, the external extremity of which is cut obliquely and just reaches the surface of the solution in the bath. The flask is kept in the latter for exactly an hour and is then allowed to cool.

At the same time 10 c.c. of the standard solution are treated similarly in another flask, the two colorations of the cold liquids being compared in the colorimeter. Since the depth of the coloration is not proportional to the quantity of higher alcohols present, the two colorations to be compared must not differ greatly ; if dilution of the spirit or of the standard solution is necessary, this must be made with pure 66·7% alcohol. If the liquids are kept in well-stoppered tubes in the dark, the colorations remain unchanged for some days, so that it may sometimes be convenient to prepare a series of standards with different quantities of the isobutyl alcohol.

In calculating the results, use may be made of the general formulæ given for aldehydes (p. 245), it being remembered that the standard solution corresponds with the distillation product of a solution of 0·500 gram of isobutyl alcohol in a litre of 50% alcohol when the distillation is carried

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[1] Alcohol of 66·7% strength may be prepared by adding 377·9 c.c. of distilled water to a litre of 90% alcohol. If the alcohol available is more concentrated than 90%, either (1) it is first brought to this strength (see Table XXV) and then diluted as above, or (2) the amount of water necessary to be added is deduced from the formula given in footnote 3 on p. 239.

out under the same conditions as with the spirit to be examined, namely, by distilling 100 c.c. and collecting 75 c.c.

EXAMPLE : The spirit was of 45% strength; 100 c.c. of it was mixed with 12·1 c.c. of pure 90% alcohol to give 111·8 c.c. of 50% alcohol. The coloration obtained by the treatment described above corresponded with that given by an isobutyl alcohol solution of one-half the standard concentration; since the standard corresponds with 500 mgrms. of higher alcohols per litre of 50% alcohol, the spirit under examination, at 50% strength, contains 25 mgrms. per 100 c.c. Consequently 100 c.c. of the original alcohol of 45% strength will contain

$$\frac{25 \times 111 \cdot 8}{100} = 27 \cdot 95 \text{ mgrms.}$$

of higher alcohols and 100 c.c. of anhydrous alcohol in the spirit will contain

$$\frac{25 \times 111 \cdot 8}{45} = 62 \cdot 1 \text{ mgrms.}$$

(B) RÖSE'S METHOD. This method, with modifications introduced by Stutzer and Reitmayr, is based on the varying degrees of solubility in chloroform shown by ethyl alcohol and its impurities, especially the higher alcohols usually found in impure spirit. Measurement is made of the change of volume—proportionate to the amount of impurities—produced in a definite volume of chloroform placed in contact with a definite volume of the alcohol to be examined.

Reagents. 1. Chloroform. The chloroform should be pure and dry. To obtain it in this condition, it may be shaken first with concentrated sulphuric acid, the acid layer being then separated and the chloroform washed several times with water in a separating funnel. The last trace of acid is neutralised by agitating the chloroform with a little dilute sodium carbonate solution ; it is dried by leaving it in contact with fused calcium chloride for a day and is then distilled and stored in a bottle with a ground stopper.

2. Pure alcohol. This is prepared as described on p. 244 and is brought to the strength of 30%, use being made of the formula :

$$x = 3 \cdot 2187\, a - 100\, p,$$

in which x is the amount of water to be added to 100 c.c. of pure alcohol of strength a and sp. gr. p.

Apparatus. The apparatus (fusel-oil tube) for the test consists, in the form devised by Herzfeld and by Windisch, of a pear-shaped glass vessel *see* Fig. 60) of about 200 c.c. capacity and fitted with a ground stopper. This vessel communicates with a cylindrical bulb holding about 20 c.c. by means of a uniform, narrow tube. The latter is graduated in twentieths of 1 c.c. and the graduation extends from 20 to 22·5 c.c. and occupies a length of about 18 cm., so that it is possible to estimate a hundredth of a cubic centimetre.

FIG. 60

Each time it is used the apparatus should be well cleaned with water, alcohol and ether and dried by warming it gently over a flame while a current
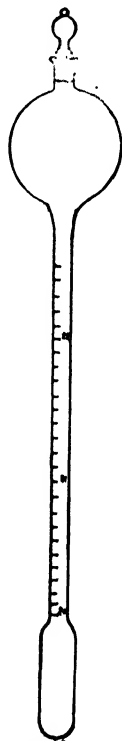
of air is blown through it by means of a long, narrow tube.   From time to time it is also necessary to clean the apparatus with a solution of potassium dichromate in concentrated sulphuric acid.

Preparation of the liquid to be tested.   The spirit must be freed from other impurities, such as esters, acids and aldehydes, which might influence the test, and is also brought to a definite strength (30%).   To this end 100 c.c. of the spirit are boiled for an hour in a reflux apparatus with a few drops of concentrated potassium hydroxide solution, the greater part of the liquid being then distilled and the distillate made up to 100 c.c.

This spirit is then brought to 30% strength by addition of pure alcohol or water.   When the spirit has a strength a (by vol.) less than 30% and a specific gravity p, the quantity x of alcohol of strength a' and sp. gr. p' necessary to bring 100 c.c. of the spirit to 30% is calculated by the following formula deduced from the general one of footnote 1 on p. 239 :

$$x = 100 \; \frac{0 \cdot 9656 \, a - 30 \, p}{30 \, p' - 0 \cdot 9656 \, a'}.$$

The volume V of the mixture thus obtained (*see* footnote 2, p. 239) will be :

$$V = \frac{100 \, a + x \, a'}{30}.$$

When, however, the spirit is stronger than 30%, the number of c.c., x, of water to be added to 100 c.c. of the spirit is given by the formula :

$$x = 3 \cdot 2187 \, a - 100 \, p,$$

where a is the strength (by vol.) of the spirit and p its sp. gr.   The volume of the mixture will be :

$$V = 3 \cdot 333 \, a.$$

Before making use of the alcoholic liquid thus diluted, it is always advisable to verify, by means of the Westphal balance, the specific gravity, which should be *exactly* 0·9656 at 15° C.

Procedure.   Two pieces of apparatus are required, for measuring the respective increases in volume of the chloroform with *pure alcohol* and with the *spirit to be tested*.   The two tubes and also the three bottles, containing the chloroform, and the 30% spirit and alcohol are placed in a suitable water-bath furnished with a good thermometer and kept exactly at 15°, and left there for a sufficient time to allow them to assume this temperature. 20 c.c. of chloroform are then introduced into each apparatus by means of a tapped funnel with a narrow stem long enough to reach the lower receptacle, care being taken not to wet the upper part or the graduated tube.   The apparatus is then placed in the bath for about 5 minutes, the chloroform being afterwards adjusted exactly to the lower mark of the graduation by adding or withdrawing a little liquid with a long capillary tube.   The inner wall of each graduated tube is dried by means of a scrap of cloth wrapped round and tied to the end of a wire.   Into one apparatus is then poured 100 c.c. of pure 30% alcohol, and into the other 100 c.c. of the spirit (also 30%) ; to each is next added 1 c.c. of pure sulphuric acid of sp. gr. 1·286 at 15° C., the apparatus being then placed again in the bath at 15° for 15–20 minutes.   The apparatus containing the pure alcohol is

tightly closed and inverted so as to obtain all the liquid in the larger bulb and then carefully brought into the original position, this procedure being repeated several times. Next, held horizontal or slightly inclined and supported by one hand on the graduated tube and the other at the neck, while the stopper is held tight with one finger, it is shaken rapidly and vigorously 150 times ; it is then placed upright in the bath at 15° and by rotating it on its axis and tapping it laterally with the finger, the whole of the chloroform is caused to sink into the lower part. The same operations are carried out with the tube containing the spirit. After the two tubes have remained for 15–20 minutes in the bath, they are raised sufficiently to read the volumes occupied by the chloroform, the differences from 20 c.c. indicating the increases in volume in the two cases.

With pure alcohol, this increase should be about 1·64 c.c.[1] Greater increases are obtained with spirits containing higher alcohols, the latter being more soluble than ethyl alcohol in chloroform. The difference between the increases in volume in the two cases, multiplied by 0·6631 (volume of amyl alcohol per 100 c.c. of 30% alcohol, corresponding with 1 c.c. of increase), gives the higher alcohols calculated as c.c. of amyl alcohol per 100 c.c. of 30% spirit.

From the number thus found the quantity of higher alcohols per cent. of the spirit under examination or per cent. of the absolute alcohol present is obtained by multiplying by $\dfrac{V}{100}$ or $\dfrac{V}{a}$. When the dilution has been made with water, it is sufficient to multiply the number found by $\dfrac{a}{30}$ and by 3·333.[2]

The results given by Röse's method are only conventional, since different higher alcohols give different increases in volume of the chloroform ; for the three principal higher alcohols, namely, amyl, isobutyl and propyl alcohols, the relative increases are approximately $1 : \frac{1}{2} : \frac{1}{3}$. Since amyl alcohol predominates and also gives the greatest increase, the results are usually calculated as amyl alcohol. Further, if the original spirit contains esters of higher alcohols, these are saponified on distillation with potash and the resultant alcohols are then estimated as higher alcohols.

5. Detection and Determination of Metals

Metals, especially copper, zinc and lead, may be found in spirits in small quantities derived from the distillation apparatus or the storage vessels. They are detected and determined by evaporating a sufficient quantity of the liquid, incinerating the residue and treating the ash by the ordinary methods of qualitative and quantitative analysis.

In particular, traces of copper may be determined colorimetrically by treating the ash with nitric acid and then rendering alkaline with ammonia. If the liquid is blue, it is compared with standard copper solution similarly

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[1] The test with pure alcohol as a comparison is to be made for each series of determinations.

[2] In some cases the higher alcohols are referred to 1 litre of alcohol, the numbers obtained as above being then multiplied by 10.

treated.   Smaller quantities may be detected by the blue coloration obtained on adding a few drops of tincture of guaiacum and potassium cyanide (*see* p. 267) to the spirit faintly acidified with acetic acid.

Finally, minimal traces of copper may be detected by adding to the liquid to be tested two or three drops of Uhlenhuth's reagent, prepared by dissolving 0 5 gram of 1 : 2-diaminoanthraquinone-3-sulphonic acid in 500 c.c. of water and adding 40 c.c. of 35% sodium hydroxide solution.   This reagent, which is red, gives a fine blue coloration in presence of copper.

6. Detection and Determination of Denaturants

The principal substances used for the denaturation of industrial alcohol are : pyridine bases, acetone and acetone oils (consisting mainly of homologues of acetone, especially methyl ethyl ketone), crude methyl alcohol and crude benzole.

A certain quantity of the spirit (e.g., 300 c.c.), together with the rinsings of the measuring vessel, is distilled with a few drops of sodium hydroxide solution or a little magnesium oxide to remove the fixed matters and the colouring materials and to liberate the pyridine bases in case these are present partly as salts ; the amount of distillate collected is that of the spirit taken.

The colourless distillate thus obtained, of which the alcoholic strength is exactly measured, is used for the following tests and determinations.

1. Detection and Determination of the Pyridine Bases. (*A*) QUALITATIVE TEST.   1. From 5 to 6 c.c. of the alcoholic distillate, which should have a strength of at least 85% (by vol.), is shaken with 2–3 c.c. of a 5% solution of anhydrous cadmium chloride in alcohol.   In presence of pyridine a white precipitate forms either immediately or after some time.

2. From 20 to 30 c.c. of the alcoholic distillate, rendered distinctly acid with dilute sulphuric acid, are evaporated on the water-bath to expel the alcohol, but should not be taken to dryness.   The residue is made alkaline with caustic soda and distilled ; the first 2–3 c.c. of the distillate (which has a marked disagreeable odour in presence of pyridine) are acidified with a few drops of concentrated hydrochloric acid and treated with 1% aqueous gold chloride solution : a pale yellow crystalline precipitate is formed if pyridine is present.   If the precipitate is washed and dried and heated with a few drops of sodium hydroxide solution in a small test-tube, the characteristic odour of pyridine is observed.

(*B*) QUANTITATIVE DETERMINATION (François).[1]   In a well cleaned, tared porcelain dish an amount of the distilled spirit containing about 0·1 gram of pyridine bases is acidified with 20–30 drops of dilute hydrochloric acid and evaporated slowly on the water-bath almost to dryness with a slight excess of 20% gold chloride solution (0·1 gram of pyridine bases requires about 0·6 gram of gold chloride).   The drying is completed in a vacuum exsiccator containing sulphuric acid, the residue being taken up in 10–15 c.c. of anhydrous ether to remove the excess of gold chloride.

After a short rest the liquid is filtered by decantation through a small

[1] *Comptes Rendus*, 1903, 137, p. 329.

filter, this treatment being repeated with fresh quantities of ether ; 50 c.c. of the latter are used in all, and the final quantity should pass through colourless. The residue remaining in the dish, consisting of the gold salt of the pyridine bases, is carefully ignited, the filter-paper being burnt in the same dish and the metallic gold thus obtained weighed when cold : gold $\times$ 0·401 = pyridine bases expressed as *pyridine*, or gold $\times$ 0·5583 = *pyridine bases*. Since the specific gravity of the latter is approximately 1, the quantity by weight indicates also the quantity by volume.

2. Detection and Determination of Ketones in absence of Alde-hydes.[1]—(*A*) Qualitative Test. (*a*) In a small cylinder with a ground stopper 5 c.c. of the distilled spirit, diluted with 20 c.c. of water, are treated with a solution of paranitrophenylhydrazine[2] prepared just when required by dissolving 0·2 gram of the hydrazine in 5 c.c. of hot 30% acetic acid, cooling and filtering so as to obtain a perfectly clear solution. In presence of ketones, a mass of yellow acicular crystals forms after 1–2 hours.

(*b*) 5 c.c. of the distilled spirit diluted, in a cylinder with a ground stopper, with 20 c.c. of water, are treated with 2 c.c. of concentrated ammonia solution and 3–4 c.c. of a solution prepared by dissolving 5 grams of am-monium iodide and 2 grams of iodine in 100 c.c. of water. If, after some hours, when the brown precipitate of nitrogen iodide has disappeared, small crystals of iodoform are observed at the bottom of the vessel, the presence of ketones is demonstrated.

(*C*) Quantitative Determination. 1. *Gravimetric method*. This con-sists in adding paranitrophenylhydrazine and thus precipitating the ketones (dimethyl and methyl ethyl) as hydrazones, which are collected and weighed.

10 c.c. of the distilled alcohol are diluted in a conical flask with 50 c.c.

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[1] The presence of aldehydes is tested for by treating 3–4 c.c. of the distilled spirit with 3–4 c.c. of Schiff's reagent. If no coloration or only a faint pink appears, the presence of aldehydes is excluded.

[2] *Paranitrophenylhydrazine* is sold by reliable makers of chemical products, while it is not difficult to prepare it in the laboratory from paranitraniline, the procedure being as follows :

Potassium sulphite solution is first prepared by saturating a solution of 10 grams of potassium hydroxide in 50 c.c. of water with sulphur dioxide in the cold and neu-tralising with powdered potassium carbonate (10 grams of potassium hydroxide and 50 c.c. of water require about 18 grams of potassium carbonate).

10 grams of finely powdered paranitraniline are then moistened in a beaker with a few c.c. of water, 21 c.c. of concentrated hydrochloric acid (37%) being added and the mass shaken vigorously and cooled in a bath of ice and salt to − 5°. A cooled solution of 6 grams of sodium nitrite in 10 c.c. of water is then added gradually and with shaking and cooling after each addition. After some time the solution is filtered rapidly through a pleated filter-paper and the filtrate neutralised, while still kept cooled, with concen-trated sodium carbonate solution and then diluted to 100 c.c.

The solution thus diluted is poured little by little into 50 c.c. of the potassium sulphite solution cooled to 0° and treated with 10 grams of potassium carbonate. The whole is shaken vigorously until a crystalline mass of potassium paranitrophenyl-hydrazinesulphonate forms, this being filtered with the help of a pump and washed with a little water. The salt is then heated in a dish with 40 c.c. of water and 40 c.c. of concentrated hydrochloric acid on a boiling water-bath for about 10 minutes. When cold the solution is neutralised by adding, little by little and with cooling, pow-dered sodium carbonate, excess of solid sodium acetate being then added. After a short rest at 0°, the paranitrophenylhydrazine which separates is pumped off, washed with a little water and dried, first between filter-papers and afterwards in the air.

of water and treated with a slight excess of the paranitrophenylhydrazine dissolved in 30% acetic acid (0·1 gram of acetone requires about 0·3 gram of paranitrophenylhydrazine dissolved in 5·6 c.c. of 30% acetic acid). After about an hour the crystalline mass formed is collected in a Gooch crucible, washed with a little 20% alcohol, dried at 105° and weighed: weight of precipitate ÷ 3·005 = weight of acetone in 100 c.c. of the sample and this weight ÷ the density of acetone (0·8) = volume of acetone in 100 c.c. of the sample. Further, multiplication of the weight of the precipitated hydrazone by 3·478 gives the ketones in 100 c.c. of the sample expressed as methyl ethyl ketone (acetone oil) and division of this value by 0·84 (mean density of acetone oil) gives the amount by volume.

2. *Volumetric method.* The ketones are treated with excess of standard iodine solution and the non absorbed iodine estimated.

Reagents. (a) Standard sodium thiosulphate solution. An approximately decinormal solution is prepared by dissolving 25 grams of the pure, crystallised salt in distilled water to a litre, the titre being determined as described on p. 41, Vol. I.

(b) Potassium iodide solution. 125 grams of the pure salt are dissolved in distilled water to half a litre, this solution being mixed with a solution of 100 grams of sodium hydroxide to half a litre.

(c) Sulphuric acid solution. 150 grams of concentrated sulphuric acid are dissolved to 1 litre; 20 c.c. of this solution should render acid a mixture of 20 c.c. of the alkaline potassium iodide solution and 10 c.c. of the hypochlorite solution (e).

(d) Starch paste (see Vol. I, p. 179).

(e) Standard sodium hypochlorite solution. 100 grams of calcium hypochlorite (with 35% Cl) are mixed in a dish with 400 c.c. of water and a boiling solution of 120 grams of crystallised sodium carbonate in 400 c.c. of water then poured on to the paste. When cold the liquid is filtered and the filtrate made up to 1 litre, 25 c.c. of 25% sodium hydroxide solution being then added.

To determine the titre of this solution, 100 c.c. of distilled water and 20 c.c. of the alkaline potassium iodide solution (b) are placed in a ½-litre bottle with a ground stopper, 10 c.c. of the hypochlorite solution being then added with constant shaking. The bottle is closed and shaken for a few moments, 20 c.c. of sulphuric acid (c) being then added and the iodine liberated titrated with the thiosulphate solution (a). The quantity of iodine liberated under these conditions by 10 c.c. of the hypochlorite solution is thus determined.

Procedure. In a ½-litre bottle with a ground stopper, 100 c.c. of distilled water, exactly 2 c.c. of the distilled spirit and 20 c.c. of the alkaline potassium iodide are shaken together, exactly 10 c.c. of the hypochlorite solution being then added and the bottle closed and shaken for a few moments. After addition of 20 c.c. of the dilute sulphuric acid the excess of unabsorbed iodine is determined by titration with the thiosulphate solution.

Subtraction of the unabsorbed iodine from the amount liberated by 10 c.c. of hypochlorite solution gives the quantity, *I*, which has reacted with the ketones in the spirit to form iodoform and from this the weight

X of ketones, expressed as acetone, in 100 c.c. of the spirit may be calculated by means of the formula :

$$X = \frac{58 \times I}{761 \cdot 5} \times 50.$$

To obtain the amount by volume, the value found is divided by the density of acetone (0·8). The results may be referred to methyl ethyl ketone by replacing in the formula the molecular weight of acetone (58) by that of methyl ethyl ketone (72), and dividing by 0·84 (mean sp. gr. of acetone oil) to obtain the quantity by volume.

EXAMPLE : 1 c.c. of the thiosulphate solution was found to correspond with 0·0255 gram of iodine, while 10 c.c. of the hypochlorite solution liberate 0·3939 gram of iodine.

Using 2 c.c. of the spirit, the excess of unabsorbed iodine is 0·1657 gram, so that the amount combining with the ketones is 0·3939 − 0·1657 = 0·2282 gram. The weight of ketones, expressed as acetone, in 100 c.c. of the spirit is thus :

$$X = \frac{58 \times 0 \cdot 2282}{761 \cdot 5} \times 50 = 0 \cdot 85 \text{ gram,}$$

which is equivalent to 1·05 c.c.

3. Detection and Determination of Ketones in Presence of Aldehydes.—(*A*) QUALITATIVE TEST. A certain amount of the distilled alcohol is diluted so as to obtain about 50 c.c. of about 50% alcohol and then boiled with 10 c.c. of 10% sodium hydroxide solution in a reflux apparatus for 15 minutes. The liquid is afterwards allowed to cool a little and then distilled, about 30–40 c.c. of distillate being collected. The distillate is diluted to 50 c.c. and boiled with 0·5 c.c. of syrupy phosphoric acid and 0·5 c.c. of colourless aniline in a reflux apparatus for about half an hour. By this treatment the aldehydes in the spirit are destroyed or fixed. After cooling to some extent, the liquid is distilled slowly, two portions of distillate of 5 c.c. each being collected and tested for ketones by one of the two methods given above (*see* p. 252). If ketones are present in more than mere traces, positive reactions should be given by both portions of the distillate.

(*B*) QUALITATIVE DETERMINATION. Exactly 25 c.c. of the distilled spirit are boiled with about 30 c.c. of water, 0·5 c.c. of syrupy phosphoric acid and 0·5 c.c. of aniline under a reflux condenser for half an hour. After cooling, the bulk of the liquid is distilled and the distillate collected in a 50 c.c. measuring flask and made up to volume with water. The ketones are then determined (*see* section 2), 20 c.c. or 4 c.c. being used according as the gravimetric or volumetric method is employed.

4. Detection and Determination of the Methyl Alcohol.—(*A*). QUALITATIVE TEST. (*a*) 25 c.c. of the spirit are slowly distilled and the first 3–4 c.c. of distillate mixed in a conical flask with 25 c.c. of water, 15–20 drops of dilute sulphuric acid and 3–4 c.c. of 1% chromic acid solution, and again distilled. The first 5–6 c.c. of distillate are discarded, the next 10 c.c. being treated with 1 c.c. of 4% phenylhydrazine hydrochloride solution, 0·5 c.c. of 4% ferric chloride solution and 2–3 c.c. of concentrated

hydrochloric acid. In presence of formaldehyde, formed by the oxidation of methyl alcohol, a crimson coloration is observed.

(b) According to the method given below under (B), a small quantity of the spirit, which naturally should not contain formaldehyde, is oxidised with potassium permanganate in presence of sulphuric acid, the excess of permanganate being destroyed with oxalic acid and the formation of formaldehyde tested for with Schiff's reagent. If, after standing for 5–6 hours, the solution has assumed a violet coloration, tending to blue, the presence of methyl alcohol is to be concluded.

When the spirit in question contains essences, perfumes, aromatic substances, etc., these should be eliminated by the method indicated on p. 258 before the test for methyl alcohol is applied.

Spirit obtained by distilling grape residues or from fruit of various kinds usually contains a small quantity of methyl alcohol and often sufficient to give the above reactions. The presence of small proportions of methyl alcohol is, therefore, not sufficient of itself to show with certainty that a spirit is derived from denatured spirit.

(B) QUANTITATIVE DETERMINATION (colorimetric). The method employed consists in oxidising the methyl alcohol to formaldehyde by potassium permanganate and sulphuric acid and adding to the solution a definite quantity of Schiff's reagent, the intensity of the bluish violet coloration produced being compared with that given under the same conditions by solutions of known content of methyl alcohol.

Reagents. 1. Schiff's reagent. 1 gram of fuchsine is dissolved in a litre of water and the solution treated with 8–10 grams of dry bisulphite dissolved in 20 grams c.c. of water and rendered acid by adding, gradually and with shaking, 20 c.c. of hydrochloric acid of D. 1·19. After a convenient rest in a well-closed vessel in the dark, the solution becomes perfectly colourless and may then be used for the test. The less the amount of bisulphite added to decolorise the fuchsine, the more sensitive will be the reagent.

2. 4 per cent. potassium permanganate solution.

3. 8 per cent. oxalic acid solution.

4. Sulphuric acid solution prepared by adding 20 c.c. of concentrated sulphuric acid to 80 c.c. of distilled water.

5. Standard solutions. These serve for the colorimetric comparison. It is useful to prepare a series of solutions corresponding with 0·25, 0·5, 0·75, 1, 1·5 and 2% by volume of methyl alcohol.

In a 200 c.c. measuring flask are placed an amount of pure methyl alcohol corresponding with exactly 2 c.c. of the anhydrous alcohol and an amount of pure ethyl alcohol (free from methyl alcohol) corresponding with 16 c.c. of anhydrous ethyl alcohol, the volume being made up with water (Solution *a*); 1 c.c. of this solution contains 0·01 c.c. of anhydrous methyl alcohol. In a second measuring flask, of 1 litre capacity, such quantity of pure ethyl alcohol (free from methyl alcohol) as corresponds with 90 c.c. of the anhydrous alcohol is made up to volume with water (Solution *b*).

In six 100 c.c. flasks are placed respectively 2·5, 5, 7·5, 10, 15 and 20 c.c. of solution *a*, the volumes being made up with solution *b*. These six solutions have a total alcoholic strength of 9% (the most convenient for the test) and contain respectively 0·025, 0·05, 0·075, 0·1, 0·15 and 0·2% of methyl alcohol; these proportions, allowing for the dilution (1 : 10) of the liquid to be tested, correspond with 0·25, 0·5, 0·75, 1, 1·5 and 2% of methyl alcohol. These solutions will be distinguished by the numbers 1, 2, 3, 4, 5 and 6.

Apparatus. For the colorimetric comparison use may be made of the ordinary arrangements for colorimetric determinations, although these are not indispensable. It is well to carry out the colour reactions in exactly similar tubes fitted with ground stoppers and having a capacity of 20–25 c.c. and a diameter of about 1·5 cm. (*see* Colorimetric Determination of Carbon in Steel, Vol. I, p. 170).

Procedure. 10 c.c. of the distilled spirit (*see* p. 251) of known alcoholic strength—which should not exceed 90% [1]—are placed in a 100 c.c. flask with sufficient pure ethyl alcohol, free from methyl alcohol, to bring the total alcohol content of the 100 c.c. up to 9 c.c. (*see* Example, below), the volume being then made up with water.

1 c.c. of the solution thus prepared is placed in one of the ground-stoppered tubes and 1 c.c. of each of the standard methyl alcohol solutions in six other tubes; 5 c.c. of the permanganate solution and 1 c.c. of the sulphuric acid are introduced into each of the tubes and the latter shaken. After about 2 minutes, 1 c.c. of the oxalic acid solution is added to each tube and the latter again shaken; carbon dioxide is liberated and the solution turns yellowish. A further 1 c.c. of the sulphuric acid solution is added and when the liquid has become colourless, 5 c.c. of Schiff's reagent, the tubes being then shaken. After 15–20 minutes there begins to appear a violet coloration due to the reaction of the formaldehyde and acetaldehyde with the Schiff's reagent, but after 5–6 hours the coloration due to acetaldehyde disappears, whereas the blue coloration due to the formaldehyde remains stable; the comparison should, therefore, be made after the lapse of the above time.

If it is found that the coloration is more intense than that given by No. 6 standard solution (which corresponds with 2% of methyl alcohol), the test is repeated with 2 c.c. of the spirit, which is made up to 100 c.c. after addition of sufficient ethyl alcohol to bring the total alcohol content to 9%. The value then obtained in the colorimetric test must be multiplied by 5.

If the quantity of methyl alcohol present in the sample is so small (less than 0·25%) that the coloration obtained is less than that given by standard solution No. 1, 100 c.c. of the spirit are distilled with a small dephlegmating column, the first 50 c.c. (exact) of the distillate being used for the colour test.

EXAMPLE: 10 c.c. (containing 5 c.c. of anhydrous alcohol) of a spirit of alcoholic strength 50% were placed in a 100 c.c. flask, together with 4·2 c.c.

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[1] If the spirit is stronger than 90%, it must be diluted, the dilution being allowed for in the calculation.

of 95% ethyl alcohol (corresponding with 4 c.c. of anhydrous ethyl alcohol) to bring the total alcoholic strength up to 9%, the whole being then made up to volume. The colour reaction is carried out on 1 c.c. of this liquid and on the standard solutions. After about 15 hours, the intensity of colour with the spirit solution is similar to that of standard solution No. 2 (corresponding with 0·5% of methyl alcohol). The methyl alcohol in the spirit amounts, therefore, to 0·5 c.c. per 100 c.c.

To refer the amount of methyl alcohol to 100 c.c. of anhydrous alcohol it is best, to avoid calculation, to make up such quantity of the distilled spirit as contains exactly 9 cm. of alcohol with water to 100 c.c. and to carry out the colour test with 1 c.c. of this solution.

EXAMPLE : If the distilled spirit in question has the alcoholic strength 41·71%, 21·58 c.c. of it (corresponding with 9 c.c. of anhydrous alcohol) are made up to 100 c.c. and 1 c.c. of the liquid thus obtained used for the colour test. If the coloration obtained is comparable with that given by standard solution No. 2 (containing 0·05% of methyl alcohol), it follows that the 9 c.c. of anhydrous spirit contain 0·05 c.c. of methyl alcohol, the amount of the latter in 100 c.c. of anhydrous spirit being then calculable by simple proportion.

The colorimetric method of determining methyl alcohol in spirit is very rapid and if the conditions are faithfully adhered to, also very exact. It is especially advantageous when the methyl alcohol is present in small amount (up to 5–6%). When, however, the methyl alcohol occurs in larger proportions, the gravimetric method is to be preferred (see p. 258).

5. Detection of Benzene and its Homologues.—The method used here is based on the transformation of benzene and its homologues into the respective nitro-derivatives, which are then reduced to amino-derivatives, diazotised and coupled with a-naphthol.

From 50 to 100 c.c. of the distilled alcohol are diluted with water to make it of about 25% strength, the liquid being then treated with a little dilute sulphuric acid and carefully distilled through a small dry condenser. The first two or three drops of distillate are dropped on to 5 c.c. of carbon disulphide in a small separating funnel and the liquid shaken with 4–5 c.c. of 10% sodium carbonate solution. The two layers are allowed to separate and the lower one, consisting of carbon disulphide with aromatic hydrocarbons in solution, washed in a second separator with a few c.c. of water and then transferred, free from drops of water, to a small conical flask.

Then drop by drop are added 2 c.c. of a mixture of 1 c.c. of fuming nitric acid with 10 c.c. of concentrated sulphuric acid, the liquid being shaken for 5 minutes, the bulk of the carbon disulphide decanted off and 10 c.c. of water poured in one lot on to the remaining acid mixture ; the rise of temperature thus occasioned suffices to volatilise any residual carbon disulphide. The decanted carbon disulphide is evaporated with 10 c.c. of water in a dish on a water-bath ; the carbon disulphide being expelled, both aqueous liquids—from the flask and from the dish—are extracted together in a separating funnel with 10 c.c. of ether. The aqueous liquid being removed, the ether is washed first with a few c.c. of water rendered alkaline with sodium carbonate and afterwards twice with a few drops of water ; it is then evaporated in a small dish at a gentle heat, the

residue being treated with 20 c.c. of water acidified with hydrochloric acid, and then with a drop of platinum chloride and 0·2–0·3 gram of zinc dust, so that evolution of hydrogen goes on for about 10 minutes.

When this ceases, the liquid is filtered and the filtrate, which should be acid, cooled to about 15° and treated with 5–10 drops of a 10% aqueous sodium nitrite solution; the acid is neutralised with sodium carbonate, cooling meanwhile, and to the liquid, which is turbid owing to the presence of zinc carbonate, are added 1–2 drops of alkaline α-naphthol solution (0·1 gram α-naphthol, 100 c.c. water, 5 c.c. of caustic soda solution of sp. gr. 1·35). If the spirit contains benzene or its homologues, an orange-red coloration is produced in consequence of the formation of an azo-colouring matter from the α-naphthol and the diazo-compound of the aniline or analogous base.

6. Detection and Determination of the Methyl Alcohol

Methyl alcohol, besides occurring in spirits derived from denatured alcohol—in which case the methods of detection and determination have already been indicated (*see* p. 254)—may also be found in larger quantities, especially in alcoholic beverages, liqueurs, etc., to which it is added fraudulently in place of ethyl alcohol. In the latter case its detection and determination require the previous elimination of extraneous fixed and volatile substances.

To eliminate the fixed substances, 100 c.c. of the sample are distilled and exactly 100 c.c. of distillate collected. To eliminate the volatile substances from the distillate, 50 c.c. of the latter are diluted in a separating funnel with 100–150 c.c. of water saturated with sodium chloride and shaken for 5 minutes with 50 c.c. of ligroin or petroleum ether. After a convenient rest, the lower layer is transferred to a distilling flask and the layer of ligroin or petroleum ether washed with 25 c.c. of brine; the lower layer is mixed with the first one and the whole distilled through a small rectifying column, the first 100 c.c. of distillate being collected in a measuring flask. The distillate, of which the alcoholic strength by volume and in grams per 100 c.c. is determined, is used for the detection and determination of the methyl alcohol.

1. Qualitative Test.—This is carried out by the method indicated for the detection of denaturants (*see* p. 254).

2. Quantitative Determination.—I. COLORIMETRIC METHOD. This is recommended especially with small proportions of methyl alcohol (up to 5–6%). To 20 c.c. of the distillate (corresponding with 10 c.c. of the original spirit), in a 100 c.c. measuring flask, is added sufficient ethyl alcohol, free from methyl alcohol, to give 9 c.c. of total alcohols in the liquid when diluted to 100 c.c.; the liquid is then made up to volume with water. The colorimetric determination of the methyl alcohol is carried out on 1 c.c. of this alcoholic solution according to the instructions given on p. 255.

2. GRAVIMETRIC METHOD. This is based on the fact that, by the action of excess of potassium dichromate and sulphuric acid, methyl alcohol is completely oxidised to water and carbon dioxide, whereas ethyl alcohol is

oxidised only to acetic acid. By weighing the carbon dioxide formed in the reaction, the amount of methyl alcohol present may be deduced.

Apparatus. Use is made of an arrangement similar to that described for the determination of carbon in iron by the Corleis method (*see* Vol. I, p. 164), this including :

1. A flask of capacity 700–800 c.c., in which the oxidation is effected ; this is closed by a ground-in reflux condenser and furnished with two gas tubes permitting of the passage of a current of air (*see* Fig. 9, Vol. I, p. 164).

2. A U-tube charged with soda-lime to purify the air admitted into the apparatus.

3. A Péligot sulphuric acid tube and a calcium chloride U-tube to dry the carbon dioxide liberated from the flask.

4. Two U-tubes containing soda-lime in the limb on the side of the flask and calcium chloride in the other limb (or the ordinary Geissler bulbs used in elementary analysis), to absorb the carbon dioxide set free in the reaction.

5. A U-tube containing calcium chloride in one limb and soda-lime in the other, to protect the absorption apparatus from the carbon dioxide of the air and from the moisture of the aspirator.

Reagents. A solution prepared by dissolving 30 grams of pure potassium dichromate, free from organic matter, in 500 c.c. of water and adding 50 c.c. of concentrated sulphuric acid.[1] The solution should be boiled for a quarter of an hour to destroy any organic matter present.

Procedure. A current of purified air is first passed through the flask, condenser and drying tubes to displace the carbon dioxide present, the absorption tubes being then weighed and inserted in place.

The spirit to be tested is then diluted so that 100 c.c. of the liquid contain not more than 12 grams of total alcohols and not more than 4 grams of methyl alcohol, exactly 25 c.c. of the diluted spirit being then introduced through the funnel of the condenser into the flask. The funnel is washed down with a little water and 500 c.c. of the chromic solution, cooled to about 5°, added ; the funnel is then closed and the flask shaken and left at rest for at least 4 hours.

After this time the condenser water is turned on and an aspirator fitted, the flask being heated very carefully to boiling, which is maintained for about an hour. The flame is then extinguished and a fairly vigorous current of air passed through the apparatus for about 15 minutes to drive out completely the carbon dioxide ; the absorption tubes are afterwards weighed : $CO_2 \times 0.727$ = weight of methyl alcohol in the 25 c.c. of liquid used and this result, divided by the specific gravity of methyl alcohol (0.7964), gives the amount by volume.

EXAMPLE : A spirit from the distillation of a liqueur, after elimination of the volatile substances (i.e., after dilution 1 : 2) contains 23.58 grams of total alcohols in 100 c.c. In order that 100 c.c. of the liquid used should contain not more than 12 grams of total alcohols, 50 c.c. of the spirit are diluted to 100 c.c. 25 c.c. of this diluted liquid give 0.7001 gram of carbon dioxide. Hence :

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[1] The purity of the reagents is established by a blank test.

Methyl alcohol in the 25 c.c. of liquid used $= 0.7001 \times 0.727 = 0.5089$ gram.

Methyl alcohol in 100 c.c. of the liquid used $= 0.5089 \times 4 = 2.035$ grams.

Methyl alcohol in the liquid from which the volatile substances were expelled, allowing for the dilution, $= 2.035 \times 2 = 4.07$ grams.

Methyl alcohol in the original spirit, allowing for the dilution made in the elimination of the volatile substances, $= 4.07 \times 2 = 8.14$ grams.

Methyl alcohol by volume in the sample $= 8.14 \div 0.7964 = 10.22\%$.

As regards this method, which is among the most exact suggested, it must be pointed out that a very small quantity of carbon dioxide is also formed by the oxidation of the ethyl alcohol, this quantity being practically constant and equal, under the experimental conditions used, to 0.01 gram of carbon dioxide per gram of ethyl alcohol present. This amount is very small and its neglect introduces only a very small error, but in exact determinations it must be taken into account. Since the quantity of the two alcohols present may be calculated sufficiently exactly by the ordinary tables used for the determination of ethyl alcohol from the density of its solutions, the correction necessitated by the presence of ethyl alcohol may be introduced by means of the formula :

$$x = \frac{C - 0.01\,A}{1.365},$$

where A is the total amount of alcohols in grams in the aliquot part used in the determination, C the amount of carbon dioxide found, and x the number of grams of methyl alcohol in the 25 c.c. of alcohol used.

It should also be borne in mind that other substances, which often accompany ethyl alcohol, e.g., certain higher alcohols, acetone, higher ketones, various essences, etc., are oxidised by chromic acid mixture with formation of carbon dioxide. These substances are, however, almost completely eliminated by the procedure indicated above.

SPECIAL PART

Industrial Spirit

As already mentioned, industrial spirit may be crude, rectified or denatured.

Crude spirits are colourless or yellowish, often slightly turbid liquids, usually somewhat acid, with a more or less unpleasant smell and taste. Rectified spirits, on the other hand, are clear, colourless, neutral, or almost so, with the smell and taste of ethyl alcohol, and do not become turbid when diluted with water. Denatured alcohol is usually yellowish or, if a colouring matter has been added to the denaturing agent, highly coloured ; the smell and taste depend on the denaturant.

Analysis of industrial alcohol is carried out by the general methods already described. As a rule, determinations of the extract and ash are useless, while that of the specific gravity may be made directly on the product, without distillation.

General Investigation of the Impurities.—The tests described among the general methods for the detection of impurities are usually long and delicate, and when it is necessary to obtain rapidly indications as to the purity of a spirit, the following preliminary tests may be used.

1. Liebig's test with potash, already described in dealing with the detection of aldehydes (*see* p. 244).

2. The sulphuric acid test, carried out without previous elimination of the aldehydes. 10 c.c. of the spirit to be tested are heated for some time with 10 c.c. of pure concentrated sulphuric acid in a wide test-tube in a bath at 120°: with impure spirit, the liquid turns brown. In this reaction the aldehydes give a somewhat more intense coloration than the higher alcohols.

3. The permanganate test. The time taken for a mixture of 50 c.c. of the spirit with 10 c.c. of 0·02% potassium permanganate solution to become decolorised or of a pale salmon colour at a temperature of about 18° is observed. With the purest alcohol, this requires about three-quarters of an hour, whilst with impure alcohols a less time is necessary—in some cases a few seconds.

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Crude spirits are characterised, besides by the bad taste, by marked quantities of volatile impurities, especially aldehydes in the more volatile fractions (foreshots) and higher alcohols in the less volatile ones (tailings or fusel oil).

By rectification these impurities are almost completely eliminated, so that, whilst in rectified spirit of passable quality the coefficient of impurity is about 40 mgrms., in well rectified spirit containing 95–97% by volume of alcohol, the coefficient of impurity does not reach 10 mgrms. As a rule these spirits contain neither aldehydes nor higher alcohols, the low coefficient of impurity being constituted mostly of acids and esters.

TABLE XXVIII

Composition of Industrial Spirits

Quality.	Alcohol, % by vol.	Volatile Impurities, mgrms. in 100 c.c. of Anhydrous Alcohol.					Coefficient of Impurity.	Author.
		Acids.	Esters.	Aldehydes.	Furfural.	Higher Alcohols.		
Rectified alcohol . .	95·6	2·5	3·6	0·1	—	2·9	9·1	Girard and Cuniasse
Good industrial alcohol	—	2·5	1·8	—	—	—	4·3	Rocques
Fine industrial alcohol	96·5	1·8	2·4	—	—	—	4·2	Royal Commission on Whisky and other Potable Spirits
Rectified alcohol . .	95·8	1·5	2·5	—	—	2	6	Central Italian Customs Laboratory
Rectified alcohol of fair quality	94·2	5	18·6	11·5	—	7·3	42·4	Girard and Cuniasse
Badly rectified industrial alcohol	93	15	55	20	1·2	70	161·2	Central Italian Customs Laboratory

FUSEL OILS

These include a group of substances formed by secondary fermentations which accompany the alcoholic fermentation and separated during the rectification of raw spirit.

They are colourless or yellowish-brown liquids and sometimes have unpleasant, irritating odours. The specific gravity is about 0·83 at 15° C. and the boiling point ranges from 80° to 160° C., the maximum distillation products being obtained at about 130°. The principal components are higher alcohols of the fatty series, mostly amyl, isobutyl and propyl alcohols. These oils do not mix with water.

A determination often required with fusel oil is the content of alcohol.

Determination of the Ethyl Alcohol in Fusel Oil.—One of the following methods is used :

(*a*) 50 c.c. of the oil are vigorously shaken for a long time with about 150 c.c. of aqueous 20% sodium chloride solution. After separation into layers, the lower aqueous one is transferred to a flask, the oily layer being shaken with a fresh quantity of salt solution and the latter, after separation, mixed with the first portion in the flask and the whole distilled. 100 c.c. of distillate are collected and the alcohol content deduced from its specific gravity at 15° C. The amount of alcohol found, multiplied by 2, gives the quantity of alcohol present in 100 c.c. of the product examined.

(*b*) 50 grams of the fusel oil are poured into a graduated cylindrical separator of about 300 c.c. capacity, the vessel in which the weighing was made being washed out with about 50 c.c. of water. 100 c.c. of water and 30 c.c. of cumene (isopropylbenzene) (b.pt. 165–168° C., sp. gr. 0·884–0·890 at 15° C.) are then added and the whole shaken vigorously for three minutes. After separation into two layers, the lower aqueous layer is placed in a dry, tared flask of about 300 c.c. capacity, the liquid remaining in the funnel being again thoroughly shaken with 20 c.c. of water and the latter subsequently added to the first portion in the flask. These operations are repeated two more times, using 20 c.c. of water in each case. The flask is weighed to determine the total weight of the aqueous liquid, which is then filtered through a dry filter, the alcoholic content of the filtrate being deduced from its specific gravity at 15°. The alcohol thus found is calculated per 100 grams of the fusel oil.

EXAMPLE : The aqueous liquid from 50 grams of fusel oil weighed 210 grams and contained 1·6% by weight of alcohol, so that the 210 grams of aqueous liquid contain $\dfrac{210 \times 1·6}{100} = 3·36$ grams of alcohol and 100 grams of the fusel oil, 6·72 grams of alcohol.

EAU-DE-VIE

Eau-de-vie (Brandy) is the product obtained by the distillation of marc or wine in such a way that the strength of the distilled spirit renders it potable, i.e., about 50%.

Analysis of these products usually includes the various determinations made on spirits (*see* General Methods). In some cases it is necessary to test for certain vegetable substances with a hot, biting taste, such as various kinds of pepper, ginger, mustard, etc., which it is customary to add to dilute eaux-de-vie (sometimes below 30%) to increase their apparent

alcoholic flavour.   These substances are detected as with vinegar (p. 226), 200–400 c.c. of the sample being used.

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The *composition of eaux-de-vie* as regards the *coefficient of impurity* is very variable and depends especially on the state of preservation and fermentation of the original marc.   In general this coefficient is very high, being not less than 350 mgrms. and rising sometimes to 1800 ; in normal products, however, it is about 700–800 mgrms.

TABLE XXIX

Compositions of Eaux-de-vie

Quality.	% of Alcohol by Vol.	Volatile Impurities, mgrms. in 100 c.c. of Anhydrous Alcohol.					Coefficient of Impurity.	Author.
		Acids.	Esters.	Aldehydes.	Furfural.	Higher Alcohols.		
Auvergne . .	49·7	72·4	272·7	266	1	243	855·1	Rocques
Burgundy . .	51·5	104·8	205·9	93	0·8	120	524·5	Rocques
Portuguese .	50	259·2	549·1	100	0·5	100	1008·8	Mastbaum and Cardoso Pereira
Piedmont . .	42·57	250	452	47	present	453	1202	Central Italian Customs Laboratory
Piedmont . .	43·66	26	192	24	present	380	622	Do. do.

BRANDY (COGNAC)

Cognac is spirit distilled from wine so that it retains the various volatile substances largely constituting the bouquet of the wine, and stored and aged for a longer or shorter time in wooden (oak) casks ; by dissolution of extractive tannin substances from the wood it assumes the well-known amber-yellow colour.

The analysis of cognac is carried out by the general methods already described ; in some cases it is necessary also to investigate the colouring matters, the following procedure being employed.

Investigation of the Colouring Matters.—The yellowish colour of brandy is due, as stated, to tannin substances derived from the wood, and these may be recognised in general by the coloration they give with ferric chloride and by the precipitate they yield, after evaporation of the alcohol, with a solution of gelatine.   To ascertain if the tannin is obtained from the oak, the following test may be made : to 10 c.c. of the spirit is added, drop by drop and without shaking, a solution of 5 grams of ferrous sulphate and 5 grams of ferric chloride in 100 c.c. of water.   With oak tannin a bluish-black coloration is obtained.

Cognac may also be coloured by addition of other substances, especially caramel or artificial organic colouring matters.

Caramel may be detected by Amthor's reaction : To 10 c.c. of the spirit

are added 30–50 c.c. of paraldehyde and then 15–25 c.c. of absolute alcohol to cause the two liquids to mix. After 24 hours, any caramel present is deposited on the walls of the vessel, to which it adheres. The liquid is then poured away, the insoluble residue dissolved in water and the solution concentrated on a water-bath to about 1 c.c., filtered and heated with phenylhydrazine solution (2 grams of phenylhydrazine hydrochloride and 3 grams of sodium acetate in 20 grams of water) : a yellowish-brown precipitate soluble in ammonia and reprecipitated in flocks when the ammoniacal solution is treated with dilute hydrochloric acid, serves to confirm the presence of caramel.

To ascertain if the cognac is coloured with *artificial organic colouring matters*, the alcohol is evaporated off, ammonia solution added and the liquid extracted with amyl alcohol ; evaporation of the amyl alcohol gives the colouring matters, which may be detected by their characteristic reactions and by dyeing tests with wool in acid or alkaline solution (*see also* Wine, and Colouring Matters).

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Composition of cognac : Whilst the original spirit distilled from wine and used for the production of cognac is usually of 60–70% strength, the *alcoholic strength* of ordinary commercial cognac is, on the average, 45–50%, the principal physical change occurring during ageing being diminution of the alcoholic content, this being related directly to the temperature and to the nature and dimensions of the storage cask. With casks of new oak holding 500–600 litres, it was observed in the Charente [1] that at a mean temperature of 15°, the diminution of alcoholic strength was 8·75% in the first year, 5% in the second and in the third year, 3·75% in the fourth and in the fifth year, and 2·5% in each succeeding year.

The *extract* of cognac, disregarding the small quantity of sugars (about 10 grams per litre) often added, varies from 0·5 to about 3–4 grams per litre in very old products ; it consists essentially of the tannin substances from the cask.

Genuine cognacs are usually rich in volatile impurities, the *coefficient of impurity* permitting of their distinction from non-genuine samples prepared from rectified industrial spirit ; this coefficient usually exceeds 300 mgrms. and may be 600–700 in very old products.

The important changes occurring during maturation are briefly as follows : The coefficient of impurity continually increases, mainly by augmentation of the oxidation products, i.e., acids and aldehydes. The esters and higher alcohols undergo no marked alteration, their proportions alone increasing indirectly with diminution of the alcoholic strength of the liquid ; in good cognacs their sum amounts to 250–350 mgrms. per litre, the higher alcohols being very rarely below 100 mgrms. Thus, according to Rocques, the ratio between higher alcohols and esters in genuine, well-prepared cognacs will lie between 1 and 2 and in the neighbourhood of 1 ; there are, however, good commercial products in which the ratio is much higher than this figure and even exceeds 3, while a value much below 1 is obtained with products containing added artificial essences, these consisting principally of esters.

In judging cognacs, Lusson suggests the use of the *coefficient of oxidation*, representing the proportion in which oxidation products (acids and aldehydes) occur in the coefficient of impurity ; this coefficient increases with the age of

[1] Rocques : *Eaux-de-vie*, 1913, p. 88.

the product. According to Lusson, the value of such coefficient—for French cognacs at any rate—is about 10 for recently distilled products and rises to 36 for very old products, but a still greater value would indicate a non-genuine brandy.

In *artificial cognacs*, the coefficient of impurity is very low and often almost zero—with well-rectified spirits, diluted with water, sweetened and perfumed somewhat with sugar and vanillin and coloured suitably. Sometimes essences are used in the preparation of these products and in such cases the coefficient of impurity consists principally of esters.

It must, however, be pointed out that special flavourings now sold for the manufacture of cognac consist of a mixture in suitable proportions of synthetic products, especially aldehydes, esters, and higher alcohols. When added to rectified alcohol, these impart to it a composition similar to that of genuine brandy. Finally, the coefficient of impurity does not serve to distinguish between brandies and products obtained from raw spirit, but in such cases tasting gives fairly certain indications.

TABLE XXX

Composition of Various Cognacs

Quality.	Alcohol, percentage by Volume.	Extract in parts per 1000.	Volatile Impurities, mgrms. per 100 c.c. of Anhydrous Alcohol.					Coefficient of Impurity.	Author.
			Acids.	Esters.	Aldehydes.	Furfural.	Higher Alcohols.		
French	51·5	12·36	149	133·2	25·5	1·6	166·3	475·5	Girard and Cuniasse
Grande Champagne, 1834	45·0	10·60	234·6	74·3	44·7	1·9	347·7	703·2	Do.
1873 Vintage . . .	59·0	1·80	138·3	120·2	40·1	2·5	304·6	605·7	Rocques
French of good quality	47·3	5·16	87·5	109·1	23·7	3	160·0	383·3	Do.
	46·8	6·68	96·1	110·9	23·7	2·5	152·0	385·2	Do.
Do. do. .	43·0	18·56	57·2	105·6	20·0	2·5	162·5	347·8	Do.
Choice French . .	46·90	10·2	30·0	117·0	20·0	1·8	251·0	419·8	Central Italian Customs Laboratory
Do. do. . .	47·56	9·5	51·7	96·3	22·0	2·0	224·0	396·0	Do.
Choice French, 70 years old . .	43·17	12·6	75	159·0	40·5	1	497·0	772·5	Do.
Conegliano . . .	48·4	—	89	161·9	11·7	0·4	234	496·9	Meloni (1891)
Sicilian	45·3	—	161	119·6	10·4	1·1	252·8	544	Meloni
Do.	45·53	8·90	20·0	201·8	37·2	0·7	226	485·7	Central Italian Customs Laboratory
Sardinian . . .	48·15	2·08	79	199	23·8	1·5	249	552·3	
Piedmontese . . .	49·50	14·5	29·0	99·6	57·5	2·9	332	521·0	

RUM

Rum is obtained by distillation of the fermented juice of cane-sugar or more frequently from cane-sugar molasses. It is a yellowish-brown or reddish liquid with special odour and taste. The analysis is carried out by the general methods already given. It is also necessary to test for extraneous colouring matters (caramel and aniline colours), the method used for cognac being followed. Further, if the amount of extract is large, the sugars—especially saccharose and invert-sugar—should be determined as described for liqueurs.

FRUIT SPIRITS

Table XXXI

Composition of Genuine Rums

Quality.	Percentage of Alcohol by Volume.	Extract in parts per 1000.	Volatile Impurities, mgrms. per 100 c.c. of Anhydrous Alcohol.					Coefficient of Impurity.	Author.
			Acids.	Esters.	Aldehydes.	Furfural.	Higher Alcohols.		
Martinique . . .	55·5	3·92	242·1	130·2	18·3	1·3	96·2	488·9	Girard and Cuniasse
Old Jamaica . . .	52·0	4·80	251·5	382·0	19·0	4·8	44·9	702·2	Rocques
Martinique . . .	58·2	—	265·2	542·1	20·0	1·5	26·3	855·1	Simon
Do. . . .	54·1	—	103·4	88	20·0	3·7	340·0	555·1	Do.
Do. . . .	56·7	—	73·2	49·3	15·4	1·0	170·0	308·9	Do.
Do. (from molasses)	—	—	201·3	443	92·0	8·8	67·5	813·1	Bonis
Do. (from cane-sugar)	—	—	83·4	68·6	18·6	1·8	214·0	380·4	Do.
Guadeloupe . . .	59·4	10·56	78·2	36·9	32·1	1·4	304·0	452·6	Sanarens
Réunion	60·3	—	177·6	70·4	15·6	1·4	224·0	489·0	Rocques
Jamaica	—	—	76·5	397·3	28·7	6·3	162·6	671·4	Royal Commission on Whisky and other Potable Spirits (London, 1909)
Do.	—	—	59·6	93·5	24·3	3·1	145·0	325·8	

The *alcoholic strength of genuine rums* usually lies between 50% and 80%, but such a high strength is generally diluted before the spirit is brought into consumption. Jamaica rum is usually quoted in commerce on a basis of 74% and that of the French colonies on 54%.

The *coefficient of impurity* of genuine rums, although always high, varies considerably with the origin and method of preparation. According to Simon's analyses,[1] genuine Martinique rums exhibit coefficients between a minimum of 300 and a maximum of 860. Bonis [2] confirms these limits for Martinique rums, the minimal values being obtained with rums distilled from fermented sugar-cane juice and the maximal ones with those obtained by distilling molasses. A knowledge of the coefficient of impurity usually permits of the distinction of genuine rums from those mixed with rectified alcohol and from artificial products prepared from industrial alcohol by addition of aromatic substances, and a little sugar and colouring matter (usually caramel).

FRUIT SPIRITS

The most important of these are obtained from nut-fruits, e.g., *kirsch-wasser* or wild cherry spirit, prepared by distilling the fermented whole or crushed fruit, and *Quetsch*, Zwetschenbranntwein and Slivovitz, derived from plums. *Cider spirit* is obtained by distilling the residues from this beverage.

The methods of analysis are those used for other spirits; in addition, for nut-fruit spirits, hydrocyanic acid and benzaldehyde and sometimes nitrobenzene are tested for and determined as follows:

1. Detection and Determination of Hydrocyanic Acid.

(*A*) Qualitative Test. (*a*) *Free hydrocyanic acid.* About 5 c.c. of the liquid are shaken in a test-tube with a few drops of fresh alcoholic

[1] *Ann. des Falsifications*, 1909, p. 394. [2] *Ibid.*, 1909, p. 521.

guaiacum tincture (0·1 gram of the resin in 50 c.c. of alcohol and 50 c.c. of water) and 2 drops of 0·1% copper sulphate solution : in presence of hydrocyanic acid, a blue coloration develops. If the colour appears before the copper salt is added, the spirit contains both hydrocyanic acid and copper.

(b) *Combined hydrocyanic acid.* About 5 c.c. of the spirit in a test-tube are rendered alkaline with a few drops of 10% caustic soda solution, the liquid being left at rest for 3–5 minutes and then faintly acidified with acetic acid ; the subsequent procedure is as in (a). If both free and combined hydrocyanic acid is present, the blue coloration will now be more intense than that obtained as in (a).

(B) QUANTITATIVE DETERMINATION. In spirits from nut-fruits, the hydrocyanic acid is partly free and partly combined with benzaldehyde (cyanohydrin). That in the latter form is determined indirectly as the difference between the total and free amounts.

Free hydrocyanic acid is determined thus : 100 c.c. of the spirit are treated in a 300 c.c. flask with a known amount in excess of standard silver nitrate solution (either N/50-solution, 1 c.c. of which corresponds with 0·00054 gram HCN, or a solution of 3·149 grams AgNO$_3$ per litre, 1 c.c. then corresponding with 0·0005 gram HCN), the liquid being diluted to the mark with water, shaken, left to settle and filtered through a dry filter. To 100 c.c. of the filtrate, slightly acidified with nitric acid, are added 5 c.c. of cold saturated ferric alum solution, the excess of silver being titrated with ammonium thiocyanate solution (corresponding in titre with the silver nitrate solution used) until the red coloration disappears. From the volume of silver nitrate solution used up by the hydrocyanic acid in 100 c.c. of the spirit, the amount of the acid is easily calculated.

The *total hydrocyanic acid* is determined similarly, but after the cyanohydrin of benzaldehyde has been decomposed. For this purpose, 100 c.c. of the spirit in a 300 c.c. flask are rendered strongly alkaline with ammonia and then treated with a measured excess of the silver nitrate solution. The whole is shaken, immediately acidified with dilute nitric acid and diluted to the mark, an aliquot part of the filtered liquid being then treated as in the determination of the free hydrocyanic acid.

The *combined hydrocyanic acid* = total less free acid, and 1 gram of combined hydrocyanic acid = 4·92 grams of benzaldehyde cyanohydrin.

The above methods cannot be used if the spirit contains chlorides, as may happen if it has been broken down with water containing these salts. In this case the total hydrocyanic acid may be determined by distilling 100 c.c. of the spirit and collecting at least three-quarters (which will contain all the hydrocyanic acid present) in a dilute solution of silver nitrate of known titre. The liquid is then made up to a definite volume and filtered, the excess of silver in an aliquot part of the filtrate being titrated with thiocyanate as already described. The free hydrocyanic acid, in presence of chlorides, should be determined colorimetrically as follows : a solution of about 0·05 gram of potassium cyanide per litre is prepared and its exact content of HCN determined by titration with silver nitrate and ammonium thiocyanate. In a series of test-tubes are placed such quantities of this

solution as, when diluted to 10 c.c., give liquids containing 2–10 mgrms. (or more) of HCN per litre, a drop of dilute acetic acid being then added. In another tube are placed 10 c.c. of the spirit to be tested. Into each tube are then poured 3 drops of guaiacum tincture (0·1 gram of the resin in 50 c.c. of alcohol and 50 c.c. of water) and 2 drops of 0·1% copper sulphate solution. Each tube in turn is closed with the thumb and inverted once, the colours being then compared. The results thus obtained are fairly accurate.

2. Determination of the Benzaldehyde.—Use is made of Cuniasse and Raczkowski's method,[1] which is as follows : 200 c.c. of the spirit, rendered alkaline with a few drops of caustic potash solution, are distilled, as much as possible of the distillate being collected in a flask holding about half a litre ; 3–4 c.c. of Fischer's reagent, prepared freshly and from pure materials (2 grams of phenylhydrazine hydrochloride and 3 grams of sodium acetate in 20 grams of distilled water), are then added and the liquid shaken and diluted with water to about 400 c.c. After standing for about two hours in a cool place, the liquid is filtered and the precipitate washed on the filter with cold water containing a little alcohol. The precipitate is then dissolved on the filter in absolute alcohol, which is added in portions of about 10 c.c. until solution is complete, the alcoholic solution being collected in a tared glass dish. The alcohol is then evaporated off in a vacuum and the residue, consisting of benzaldehydephenylhydrazone, weighed : this weight × 0·54 = benzaldehyde in the 200 c.c. of spirit taken.[2]

3. Detection of the Nitrobenzene.—This is reduced by means of zinc and hydrochloric acid and the aniline thus formed liberated by addition of alkali, extracted with ether and tested by its special reactions, e.g. :

(a) The aqueous solution gives with calcium hypochlorite a violet-red coloration, gradually becoming reddish.

(b) The solution in concentrated sulphuric acid gives a blue colour with a drop of potassium bichromate solution.

(c) The acid solution is coloured blue by addition of a small quantity of potassium chlorate.

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The mean *alcoholic strength* of *kirschwasser* is about 50%.

The *coefficient of impurity* varies from 350 to more than 1500 mgrms. and the esters preponderate greatly over the higher alcohols, so that the ratio, higher alcohols : esters is always less than unity and thus different from that obtained with wine spirits. The same holds for cider spirit.

Hydrocyanic acid is a characteristic component of kirschwasser and varies in amount from 20 to 90 mgrms. per litre. The acid is mostly free in new kirschwasser, but tends to combine as the spirit ages.

Prepared kirschwasser is made either by distilling a mixture of neutral alcohol with fermented cherry juice or by distilling the fruit which has been allowed to

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[1] *Monit. Scientifique,* 1894, p. 915.

[2] If the spirit contains small quantities of extractive matters, the following method may also be used : 100 c.c. of the spirit are treated in a flask holding about 400 c.c. with 2 c.c. of Fischer's reagent and shaken ; 200 c.c. of water are then added and after 2 hours the liquid is filtered, the precipitate being treated as described above.

ferment in presence of sugar. It is not easy to distinguish these products by analysis.

Artificial products, obtained by addition of aromatic substances to commercial alcohol, may however be recognised, as they contain little or no hydrocyanic acid and are rich in benzaldehyde. Kirschwasser and similar spirits are prepared, although rarely, from alcohol and bitter almond or cherry laurel water and in such cases hydrocyanic acid is present. Artificial products are generally prepared from rectified alcohol and thus have a low coefficient of impurity and contain only very small amounts of higher alcohols.

From the *hygienic* point of view, kirschwasser, etc., should contain not more than 0·005% of total hydrocyanic acid, no added nitrobenzene and no injurious metals. Small quantities of *copper* (up to 0·04% is allowed) are, however, nearly always present in kirschwasser and sometimes traces of *zinc*.

Plum spirit always has a very high coefficient of impurity and contains less hydrocyanic acid than kirschwasser.

The coefficient of impurity of *cider spirit* is also very high, namely, 450–800 mgrms. ; here too the ratio, higher alcohols : esters is very low.

TABLE XXXII

Compositions of Fruit Spirits

Quality.	Percentage of Alcohol by Volume.	Extract in parts per 1000.	Volatile Impurities, mgrms. per 100 c.c. of Anhydrous Alcohol.					Coefficient of Impurity.	Author.
			Acids.	Esters.	Aldehydes.	Furfural.	Higher Alcohols.		
Kirschwasser . . .	45·3	2·16	100·6	209·8	8·5	0·3	110·3	429·5	Girard and Cuniasse
Do. . . .	49·9	1·64	51·0	184·0	8·0	0·3	89·2	341·1	Saglier
Do. . . .	49·5	—	133·2	411·8	6·9	0·2	162·0	714·1	Rocques
Do.	50·2	—	171·6	337·9	14·1	0·6	175·0	699·6	Do.
Amarene Kirschwasser	55·2	—	141·0	266·0	12·0	0·5	140·0	559·5	Roux and Bonis
Saumur Quetsch . .	60·5	0·76	63·0	155·0	26·0	1·8	288·0	533·8	Riche
Hungarian Slivovitz .	50·06	0·54	105·4	123·4	7·6	1·2	30·6	268·2	Mausfeld
Quetsch . . .	48	—	316·2	536·8	8·1	0·1	311·1	1172·3	Rocques
Do. . . .	47·1	—	374·7	368·7	6·4	—	210·0	959·8	Do.
Cider Spirit . . .	48·5	1·28	163·2	235·8	61·5	1·6	172·1	631·2	Girard and Cuniasse
Do. . . .	64·9	0·14	25·9	639·6	16·0	0·8	169·8	852·1	Rocques
Do. . . .	68·6	0·39	99·6	398·3	20·0	0·9	103·0	621·8	Do.
Pear Spirit . . .	65·5	1·20	84·2	274·0	7·6	0·4	299·5	665·7	Do.
Do. . . .	63·7	0·42	96·0	506·4	12·6	0·6	136·0	751·6	Do.

CEREAL SPIRITS

The most important of these are *whisky* and *gin*. By *whisky* is meant the distillation product of the fermented worts obtained by diastatic saccharification of various cereals. Good whiskies are prepared by partial rectification of the first distillate. *Gin* is similarly prepared, but juniper berries are added to the still ; thus, it contains juniper oil as well as the ordinary impurities of alcohol.

The analyses of these products are carried out by the ordinary methods.

TABLE XXXIII

Compositions of Whisky and Gin

Quality.	Percentage of Alcohol by Volume.	Extract in parts per 1000.	Volatile Impurities, Mgrms. per 100 c.c. of Anhydrous Alcohol.					Coefficient of Impurity.	Author.
			Acids.	Esters.	Aldehydes.	Furfural.	Higher Alcohols.		
Whisky	47·6	2·52	65·5	52·8	20·0	0·4	188·0	326·7	Rocques
Do. (4 years old).	—	—	27·3	39·6	8·3	1·1	337·8	414·1	Royal Commission on Whisky and other Potable Spirits, 1909
Do. (10 years old)	—	—	68·4	41·5	11·0	1·5	361·8	484·2	
Do. (Scotch) . .	49·4	2·34	31·5	93·0	9·8	3·3	300·0	437·6	
Gin	40·7	—	57·7	98·0	12·2	1·7	157·5	327·1	
Do.	43·4	—	10·5	105·0	1·7	1·7	105·0	223·9	
Do.	47·5	0·52	40·4	18·5	9·9	0·3	27·9	97·0	Girard and Cuniasse

LIQUEURS

These are spirituous beverages, sometimes containing sugars, and flavoured with essences or aromatic plant juices.

They vary widely in composition, but in general may be divided into : *Liqueurs free from sugar*, such as *absinthe* ; *liqueurs containing sugars and bitter substances*, termed *bitters*, and *true liqueurs*, which contain sugars and essential oils or vegetable extracts.

Besides the tests and determinations already indicated among the general methods (the tasting, determination of the specific gravity and the tests relating to volatile impurities and to denaturants, are made on the distillate, freed if necessary from essential oils), analysis of liqueurs includes the following.

1. Determination of the Sugars.—Usually liqueurs contain only saccharose, but in some cases they may contain also invert sugar and starch glucose.

A little of the liqueur is freed from alcohol by evaporation and then clarified with lead acetate. If a few c.c. of the remaining liquid then give no reduction, the saccharose is determined in the saccharimeter. If, however, reduction does occur, the saccharose is determined by inversion and calculated by Clerget's formula, and the reducing sugars are estimated by Fehling's solution (*see* this volume, Sugars : General Methods).

2. Detection of Artificial Sweetening Materials.—The sweetening agents especially looked for in liqueurs, particularly if these are poor in sugar, are saccharin (orthobenzoicsulphinide, $C_6H_4 \left\langle \begin{smallmatrix} CO \\ SO_2 \end{smallmatrix} \right\rangle NH$) and its sodium salt or crystallose, and dulcin or sucrol (paraphenetolecarbamide, $NH_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot O \cdot C_2H_5$).

(*A*) DETECTION OF SACCHARIN.—100 c.c. of the liqueur are freed from alcohol by heating on a water-bath,[1] the residual liquid being diluted to

[1] If the liqueur has been prepared with vegetable infusions or extracts, it is sometimes convenient to submit it to preliminary defecation so as to facilitate the extraction

100 c.c. with water, introduced into a separating funnel, acidified with 10 c.c. of dilute phosphoric acid (1 : 3) and shaken several times with 100 c.c. of a mixture in equal volumes of (1) ether and petroleum ether boiling below 70°, or (2) ether and benzene. It is next left at rest for about 12 hours and then again shaken three or four times; after separation into two layers, the aqueous acid liquid is withdrawn. The ethereal solution is left for some time, after which the funnel is shaken somewhat so that most of the drops of aqueous acid on the walls collect below the ethereal liquid and can then be separated almost completely. The ethereal liquid is then shaken vigorously with 2–3 c.c. of distilled water, which is subsequently separated as above. The washed ethereal liquid is filtered into a flask and the funnel and filter washed with a little of the ethereal mixture.

If a more complete extraction of the saccharin is desired, the aqueous acid liquid may be again extracted once or twice, 50 c.c. of the ethereal mixture being used each time; but even this treatment does not result in the total extraction of the saccharin.

From the united ethereal liquids the bulk of the solvent is distilled off, the liquid residue and the washings of the flask with a little of the distillate being evaporated in a dish at a gentle heat on a water-bath. The residue thus obtained is dissolved in a little hot water and treated with a potassium permanganate solution of about normal strength, this being added little by little to destroy any extraneous substances extracted together with the saccharin. The addition of permanganate is continued until the liquid assumes a persistent pink coloration, the mixture being kept at about 100° C. during the treatment.

The aqueous liquid thus obtained is filtered and acidified with a few drops of dilute phosphoric acid and then repeatedly extracted with 50 c.c. of ether. The united ethereal liquids are washed with two quantities of 2–3 c.c. of water, as indicated above, and then filtered through a small dry filter into a tared glass dish and, together with the few c.c. of ether used to wash the filter, evaporated on a water-bath at a gentle heat and the residue weighed.

This residue may be identified as saccharin by the following tests :

(a) In the first place by its peculiar, very persistent sweet taste.

(b) If in sufficient quantity to crystallise, by its m.pt., which, with pure saccharin, is 223–224°; the commercial product and that obtained by the above procedure, if not well crystallised, melt at a rather lower temperature.

(c) By transformation into salicylic acid. Part of the residue is treated with a little concentrated sodium (not potassium) hydroxide solution, the

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of the saccharin and to prevent the formation of an emulsion. For this purpose the alcohol-free liquid is heated to boiling and rendered distinctly acid with 20 drops of concentrated acetic acid and then shaken and cooled in a current of water. To the liquid, thus cooled, are added 10 c.c. of 20% neutral lead acetate solution and, after standing for half an hour, the excess of lead is removed by means of 20 c.c. of a solution prepared by mixing equal volumes of 20% sodium sulphate and 20% sodium phosphate solutions. The precipitate formed is allowed to settle and the liquid then filtered, the filtrate being acidified with phosphoric acid and used for the detection of saccharin as above. For quantitative determination, definite volumes are employed.

water being then evaporated and the residue heated for half an hour in an oil- or paraffin-bath at 250° C. When cold the mass is taken up in water and acidified with sulphuric acid, the salicylic acid thus formed being extracted with ether and detected in the residue left after evaporation of the ether by the characteristic violet coloration given with a few drops of dilute ferric chloride solution.

(*d*) By testing for sulphur. Part of the residue is gently fused with a convenient quantity of a mixture of dry sodium carbonate and pure nitre. The product is dissolved in water, acidified with dilute hydrochloric acid and tested with barium chloride.

(*B*) DETECTION OF DULCIN. The following method is used for the detection of dulcin or sucrol : 100 c.c. of the liqueur are mixed with about 5 grams of lead carbonate and evaporated at a gentle heat to a paste, which is immediately treated with concentrated alcohol ; the alcoholic liquid is separated and the residue washed repeatedly with alcohol. The united alcoholic liquids are filtered, the filtrate being evaporated slowly to dryness on a water-bath and the residue extracted with ether. Evaporation of the latter then yields almost pure dulcin, which may be recognised, besides by the sweet taste and melting point (173°), by the following reaction due to Ruggeri [1] : To a small quantity of dulcin, in a porcelain dish, are added about 2 c.c. of 6% silver nitrate solution or of 5% mercuric chloride solution, the liquid being then evaporated and frequently stirred with a glass rod to complete dryness. If the dish is still left for some time on the water-bath, there appears at the bottom a violet coloration, which becomes more intense if the dish is heated for a short time on a sand-bath at 160°, particularly if mercuric chloride were used. Finally, if the dish is taken from the bath and absolute alcohol added while it is still hot, the liquid assumes an intense and permanent wine-red coloration.

3. Investigation of the Bitter Substances.—For the complete investigation of the various injurious bitter principles, reference must be made to the special articles in books dealing with the subject.[2]

4. Determination of the Essential Oils.—This is effected by a method [3] which includes distillation of the liqueur to eliminate more especially the sugars, extraction of the essences from the alcoholic distillate by means of petroleum ether in presence of salt, and evaporation of the ether under definite conditions.

Procedure. Into a separating funnel of about 300 c.c. capacity are introduced successively 50 grams of recrystallised and finely powdered common salt, 200 c.c. of the alcoholic distillate brought to about 25% strength and 10 c.c. of petroleum ether of b.pt. about 40° C. The whole is shaken until the salt is completely dissolved and then for about ten minutes longer. In this salt solution the essences are almost entirely insoluble and they are dissolved in the petroleum ether, which is easily separated from the salt liquid owing to the marked difference in specific gravity.

[1] *Annali del Lab. chim. centr. delle Gabelle,* 1897, III, p. 138.

[2] Girard, *Analyse des Matières aliment.,* 1904, p. 223 ; Koenig, *Nahrungs- und Genussmittel,* 1910, Vol. III, p. 302 ; Allen, *Commercial Organic Analysis,* Vol. VII, p. 137.

[3] Muttelet, *Ann. des Falsifications,* 1906, p. 17.

When the ethereal layer is separated, the salt solution is transferred to a second separator similar to the first and there treated with a further 5 c.c. of petroleum ether. This treatment is repeated a second time in the first separating funnel, the use of the latter diminishing the loss as far as possible. The collected ethereal liquids are dried with a little anhydrous sodium sulphate and transferred to a tared conical flask of such capacity that they form a shallow layer of considerable extent. By means of a cork carrying two glass tubes a gentle stream of air is passed through the flask, which, during the early stages of the evaporation, is placed in a bath at about 25° C. to diminish the fall of temperature due to the evaporation of the ether.

After the bulk of the solvent has evaporated, the flask is weighed every five minutes until consecutive losses in weight become equal. With good working, the losses may be reduced to 1–2 milligrams, five or six weighings being usually required. The weight of essence obtained is referred to a litre of the liqueur.

5. Detection of Colouring Matters.—Liqueurs are often coloured, especially yellow, green or red. With a yellow liqueur, tests are made more particularly for tannin substances, caramel and artificial organic colours, the methods already indicated being followed (*see* Brandy, Wine). A green colour may be due to chlorophyll if obtained by infusion of vegetable matters, but is more often due to artificial organic colouring matters. Red may be produced by cochineal or by coal-tar colours.

In testing for cochineal, the liqueur is diluted with water and acidified with acetic acid, the liquid obtained being then shaken with amyl alcohol. The alcoholic layer is separated and evaporated with addition of a little water, the residue being treated with a few drops of 3% uranium acetate solution. In presence of cochineal, a bluish-green coloration or precipitate is produced, this changing to orange on addition of an acid.

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In considering the results of analysis of a liqueur, account is taken of its nature and quality and also of the quality of the alcohol used in its manufacture, this being deduced up to a certain point from the taste and from the chemical examination of the distilled alcohol free from essential oils.

Liqueurs should not contain artificial sweetening substances and should be free from injurious bitter and colouring matters and from harmful metals.

ESSENTIAL OILS

Essential oils, known also as *Ethereal oils*, *Volatile oils*, or *Essences*, are products of more or less complex composition, consisting mostly of mixtures of substances with widely varying chemical functions; of these substances the principal are as follows:

1. *Hydrocarbons*, rarely of the fatty series (heptane, myrcene and various paraffins), more often of the aromatic series, such as styrene and cymene, but usually terpenes, e.g. pinene, camphene, fenchene, limonene, dipentene, sylvestrene and phellandrene.

2. *Alcohols*, such as linalool (licareol, coriandrol), geraniol (lemonol, rhodinol, réuniol), citronellol (the rhodinol or réuniol of some authors), terpineol, borneol and menthol. The alcohols occur in these oils both in the free state and also in combination with acids as esters (*see* later).

3. *Aldehydes*, the most important being benzaldehyde, cinnamaldehyde, salicylaldehyde, citral and citronellal.

4. *Ketones*, such as camphor, methylheptenone, carvone, fenchone, thujone or tanacetone, pulegone and menthone.

5. *Phenols*, such as anethole, eugenol, safrole, thymol, carvacrol and chavicol.

6. *Acids, Esters*: the former sometimes occur in small quantities free (acetic, propionic, butyric, valeric and hydrocyanic acids) and more frequently in combination with the above-mentioned alcohols as esters (formic, acetic, valeric, myristic, tiglic, cinnamic, salicylic, etc., esters).

7. *Sulphur compounds*, such as alkyl thiocyanates (in mustard oil, garlic oil and the like).

Analysis of essential oils with a view to identifying them and of determining their value and purity is based on the measurement of certain physical characters, on the estimation of certain special components (esters, alcohols, aldehydes, etc.), and on tests for the various substances which are commonly used for purposes of adulteration.

These are all treated below under *General Methods*, the detailed analysis of some of the more important essential oils being then described (*Special Part*).

GENERAL METHODS.

The physical characters of greatest importance in the examination of the volatile oils are, besides appearance and odour: specific gravity, rotatory power, refractive index, solidifying point, behaviour on distillation, and solubility (*see* sections 1–7). The components most often requiring estimation are: esters, alcohols, aldehydes, ketones, phenols (*see* sections 8–11), and the most common adulterants to be looked for are: alcohol,

mineral and fatty oils, oil of turpentine and various volatile oils of little value (*see* section 12).

1. External Characters

Of special importance is the odour, which may be conveniently judged by rubbing a few drops of the oil between the hands or by moistening with it a strip of filter-paper or a piece of cotton-wool.

2. Specific Gravity

This is measured in the usual way, i.e., with a Westphal balance or picnometer, generally at 15° C.   If only a small quantity of material is available, use may be made of a small **U**-shaped picnometer (*see* Spirits, p. 233).   If a temperature other than 15° is used, the result may be corrected by means of the coefficient 0·00075, to be added for each degree above, or subtracted for each degree below, 15° C.

The sp. gr. of the ethereal oils at present known varies between about 0·8 and 1·2. Oils lighter than water are usually rich in hydrocarbons, alcohols (free or esterified), aldehydes or ketones, such as dill, angelica, orange, bergamot, caraway, citronella, coriander, cumin, eucalyptus, geranium, lavender, lemon, neroli and rose oils.   Oils with specific gravity approaching or exceeding 1 usually contain either a phenol or phenolic derivative in marked quantity or certain ethers, such as aniseed, gaultheria, clove or sassafras oil.   Volatile oils containing sulphur compounds also have high specific gravities, e.g., mignonette root oil and mustard oil.

The specific gravity of any oil is not, however, constant but is influenced by the development of the original plants, the method of preparation or purification of the oil, its age, etc.

3. Rotatory Power

This is measured with a Laurent shadow polarimeter, using yellow light and a tube 10 cm. long (for highly coloured oils, tubes 5 or 2·5 cm. long may be used).   The observation is usually made at 15° or 20° and for most essential oils the temperature has not a great influence on the rotatory power ; for lemon and orange oils (*q.v.*) it is, however, necessary to correct for temperature.   As a rule the rotation is expressed in circular degrees for a 10 cm. tube and is denoted by α or α_D.

The specific rotation, $[\alpha]_D$ may be calculated from the formula :

$$[\alpha]_D = \frac{\alpha}{l \times d},$$

where α is the observed rotation, l the length of the tube in decimetres and d the specific gravity of the oil.

If no polarimeter is available, use may be made of a saccharimeter with a Ventzke scale, the different dispersive power of the quartz with respect to essences being disregarded.   In this case the saccharimetric divisions are divided by 2·89 to obtain circular degrees.   A tube 10, 5 or 2·5 cm. long is used according to the rotatory power of the oil,

The rotatory powers of some essential oils vary within fairly wide limits. This measurement should, however, never be omitted, since it is of great use in the detection of adulteration, especially with oils of very high rotatory powers, such as lemon and orange oils.

4. Refractive Index

This is determined by means of *refractometers*, the type most commonly used being that of Abbe.[1]

The *Abbe refractometer* (Fig. 61) consists of a heavy foot carrying a tube *a* rotating about a horizontal axis, together with a graduated sector *b*. Round the same axis rotates also a system of prisms *c* joined rigidly to an arm *d* which traverses the sector *b* and serves for reading the graduations.[2] The lower part of the tube *a* consists of a graduated drum rotatable on its own axis by means of a screw *e* and containing a compensator to eliminate the dispersion involved when white light is used. Lastly the foot of the apparatus is provided with a movable mirror *s*.

The system *c* contains two prisms which join together to form a parallelepiped. Between them is placed a drop of the liquid to be examined so that when the two prisms are fitted into place the drop expands to form a thin film between them. The light rays are reflected from the mirror *s* through the system of prisms into the eye-piece *a*.
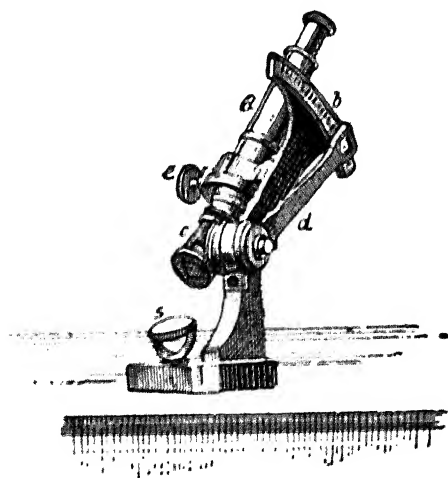
FIG. 61

In making an observation, the arm *d* is displaced so that, with total reflection at the surface of the liquid film between the prisms, the lower half of the field of vision (which is furnished with cross-webs) appears dark. In general the line of separation is coloured and hazy; the screw *e* must then be turned until this line appears as sharp and colourless as possible. The graduations of the sector and of the compensator are then read; finally the screw *e* is turned to render the line of separation colourless, this being brought back to the proper position by moving the arm *d*. The mean between the two readings of the scale of the sector *b* gives the refractive index with reference to Fraunhofer's yellow *D* line; the mean of the two readings of the compensator serves for the calculation, by means of a table supplied with the apparatus, of the dispersion between the Fraunhofer *D* and *F* lines.

[1] Other refractometers are the *Pulfrich* and the *Pulfrich immersion* instruments. The latter is easy to manipulate and gives fairly exact results, while, with the aid of a special auxiliary prism, it may also be used for very small quantities of liquid.

[2] In some of the more recent types of apparatus the system of prisms is surrounded by a double jacket, through which water at constant temperature may be circulated, as with the butyro-refractometer (see p. 36).

The index of refraction does not vary much with different essential oils, the values lying between about 1·43 and 1·62 for temperatures of about 20°; in some cases it may, however, serve for the detection of extraneous substances.

5. Solidifying Point

For the exact determination of the solidifying point of some essential oils use may be made of the apparatus shown in Fig. 62.

To a large, glass, cylindrical beaker C is fitted a metal cover with a central aperture through which passes a test-tube b; into the latter fits another test-tube a of somewhat smaller diameter but widened at the upper part. The tube a is closed with a perforated metal cover carrying a thermometer t reading to 0·5° and supported by three spring tongues conveniently fixed below the orifice in the cover.

The outer vessel is first filled with cold water and pieces of ice (for aniseed or badiana oil) or with a mixture of snow and salt (for fennel oil). The tube a is then charged with sufficient essential oil to fill it to a depth of 5 cm. and the thermometer immersed so as not to touch the walls of the tube. The oil is allowed to cool until the thermometer indicates a temperature about 5° below the presumed solidifying point of the oil, solidification being then provoked by shaking and by rubbing the walls of the tube with the thermometer. If the oil remains liquid, a fragment of the oil solidified separately is dropped in, or a crystal of anethole, the oil then setting immediately to a crystalline mass with evolution of heat. Crystallisation of the product is facilitated by continual agitation with the thermometer, the mercury column of which rises rapidly to a maximum and there stops. This maximum temperature represents the solidifying point of the oil.
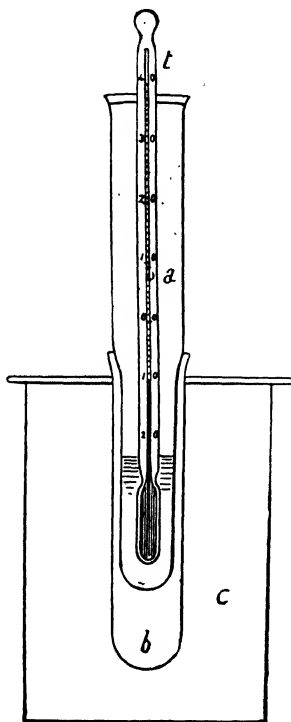
FIG. 62

Most essential oils solidify only at low temperatures, so that in practice this determination is carried out with very few oils, especially aniseed, badiana, fennel, rose and rue oils, which are rich in constituents which readily crystallise. Where it can be made the determination furnishes a valuable criterion of the value and purity of an oil.

Aniseed, badiana and fennel oils solidify easily owing to their content of anethole, the first two at 15–20° and the last at 3–6°. Rose oil (Bulgarian) solidifies at 19–24° and the German oil at 27–37°, owing to their stearoptene content. Rue oil solidifies at 8–10° as a result of the presence of methyl nonyl ketone. The higher the solidifying points of these oils, the more they are valued. Lowering of the solidifying point indicates addition of extraneous substances or the partial removal of their characteristic principles.

6. Boiling Point : Fractional Distillation

To determine the boiling point or rather the temperature limits between which an essential oil distils, an ordinary distillation flask holding 60–80 c.c. is used.

Note is made of the temperature at which the first drops begin to distil, that at which the bulk of the oil passes over and the maximum temperature at which the last portions distil. It is advantageous to keep the different fractions distilled separate, so as to make with them investigations on the constituents of the oil. In order to separate these constituents it is often useful to carry out the distillation at reduced pressure (20–40 mm.).
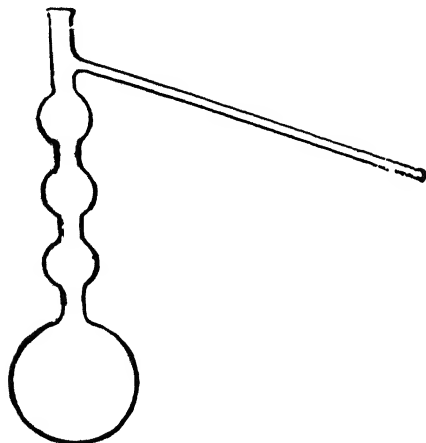
In some special cases, such as the analysis of oil of lemon and the like, the fractional distillation is carried out in a flask with a three-bulb head (see Fig. 63).

FIG. 63

Essential oils, which are composed of mixtures of different substances, have no fixed boiling point, but boil between certain limiting temperatures, often widely separated ; these limits lie between about 120° and 300°. Fractional distillation serves either to separate the various components of essential oils or to detect fraudulent practices. For instance, it is easy by distillation to detect addition of alcohol or petroleum ether, which boil below 100°. Addition of oil of turpentine may also, in many cases, be discovered by fractional distillation (see later : paragraph 12).

7. Solubility

The volatile oils are readily soluble in various organic solvents, such as absolute alcohol, ether, chloroform, benzene, carbon disulphide, benzine, paraffin oil, ethyl acetate and glacial acetic acid. In dilute alcohol they are more or less soluble according to their nature.

Of special importance in analysis is the test of solubility in 90%, 80% and 70% alcohol. The test is made in a glass cylinder graduated to 0·5 c.c. Into this is measured 1 c.c. of the oil, to which the alcohol is added, little by little and with thorough shaking, until a clear solution is obtained ; note is made of the volume of alcohol necessary. If, as sometimes happens, further addition of alcohol causes turbidity, note is made of this.

Oils rich in oxygenated substances (esters, phenols, etc.) often give turbid solutions with petroleum ether, paraffin oil or carbon disulphide, owing to separation of drops of water, small quantities of which are dissolved and retained by such oils.

In 90%, 80% or 70% alcohol, any essential oil exhibits almost constant solubility. The test of solubility in dilute alcohol gives useful indications,

especially as regards adulteration with oil of turpentine and with petroleum in oils soluble in 70% or 80% alcohol, since oil of turpentine and petroleum are but little soluble in alcohol of these concentrations. Fatty oils are detected even more easily owing to their insolubility in 90% alcohol.

8. Determination of the Esters by Saponification

Many essential oils contain esters (mostly acetates) of alcohols of the formulæ $C_{10}H_{18}O$ (borneol, geraniol, terpineol, linalool), $C_{10}H_{20}O$ (menthol, citronellol), $C_{15}H_{24}O$ (santalol). When boiled with alcoholic potash, these esters are hydrolysed (saponified) and yield the free alcohol and the potassium salt corresponding with the acid of the ester. Thus, the volatile oils containing esters have saponification numbers, which may be determined in a manner analogous to that used for fatty matters.

About 2 grams of the oil are weighed in a 100 c.c. flask and treated with 10 or 20 c.c. of N/2-alcoholic potash (usually 10 c.c. suffice, 20 c.c. being used only in cases where 10 c.c. have been shown to be insufficient). The flask is closed with a cork traversed by a glass tube about a metre long or by a small upright bulb condenser, and is then heated for half an hour on a water-bath. After cooling, about 50 c.c. of water and a few drops of alcoholic phenolphthalein solution are added and the excess of alkali titrated with N/2-sulphuric acid.

The number of milligrams of KOH necessary to saponify 1 gram of the oil represents the *saponification number* or, more accurately, the *ester number* of the oil.

If the oil contains free acid (as may happen, especially with old or badly stored oils), allowance is made for the alkali necessary to neutralise the acid in the cold, that is, the *acid number* is determined and then subtracted from the saponification number.

From the ester number the content in esters or in alcohol corresponding with the esters is calculated by the following formulæ, it being assumed that the esters are *acetates*, as is commonly the case :

$$(1) \text{ Percentage of } esters = \frac{\text{ester number} \times m}{560}$$

$$(2) \text{ Corresponding percentage of alcohol} = \frac{\text{ester number} \times m_1}{560},$$

where m and m_1 are the respective molecular weights of the acetic ester and of the corresponding alcohol.

The ester number for any essential oil may vary within more or less wide limits (*see* Table XXXIV), but its determination is of importance in the identification of an oil, the detection of adulteration, and for judging of the quality of the oil. With some oils, the esters represent the odoriferous principle, e.g., linalyl acetate in bergamot, lavender and petit-grain oils, bornyl acetate in pine-needle oil and menthyl acetate in mint oil, the value of these oils being deduced from the ester content.

The ester number also serves for the detection of fatty oils, which have very high saponification numbers.

9. Determination of the Free Alcohols (Acetylation)

The procedure followed here varies according as the alcohols occur alone or are accompanied by esters or by aldehydes or ketones.

1. Free Alcohols alone.—In this case the content in free alcohols (borneol, geraniol, terpineol, linalool, menthol, citronellol, santalol, thujyl alcohol) is determined by transforming the alcohols into the corresponding acetates by boiling with acetic anhydride and then determining the saponification number of the acetylated product (*acetyl saponification number*).

To this end, 10 c.c. of the oil are boiled for an hour with an equal volume of acetic anhydride and 2 grams of dry sodium acetate in a flask fitted with a ground-in, upright condenser. When cold, the liquid is diluted with water, heated for about half an hour on a water-bath and then transferred to a separating funnel. The acetylated oil is separated from the aqueous liquid, washed with water or sodium chloride solution until it is neutral and dried by means of anhydrous sodium sulphate. 2 grams of this acetylated oil are then employed for the determination of the saponification number as described above (p. 279).

The percentage of alcohol in the oil may be calculated by means of the formula :

$$\text{Percentage of alcohol} = \frac{a \times m}{20\,(s - a \times 0.021)},$$

where *a* c.c. of N/2-KOH have been used and *m* denotes the molecular weight of the alcohol concerned and *s* the number of grams of acetylated product used in the determination of the acetyl saponification number.

2. Alcohols with Esters.—When an essential oil contains free alcohol and also esterified alcohol, to ascertain the amount of the free alcohol it is necessary to determine the ester number (as in paragraph 8, above) on the oil as it stands and the acetyl saponification number, the *free alcohol* being then calculated by means of the above formula. The esterified alcohol (acetate) is calculated from the ester number by means of formula (2) on page 279 ; *total alcohol* = free alcohol + esterified alcohol.

This method gives exact results with borneol, isoborneol, geraniol, menthol and santalol, but does not yield reliable figures with the tertiary alcohols, linalool and terpineol. When the latter are to be estimated, the acetylation should be carried out on the oil (5 c.c.) diluted with oil of turpentine (25 c.c.), according to Boulez's method.[1]

3. Alcohols with Aldehydes and Ketones.—When an essential oil contains, besides the alcoholic compounds, also aldehydes and ketones, the determination of the alcohols by acetylation is no longer accurate, since aldehydes and ketones react with acetic anhydride. In such cases the aldehydes may be eliminated by means of their insoluble compounds with alkaline bisulphite or other reagent (*see* paragraph 10 : Detection of

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[1] *Bull. Soc. chim. de France*, 1907, Vol. I, p. 117. Instead of oil of turpentine another solvent may be employed, such as xylene, which is not attacked at all by acetic anhydride.

Aldehydes), the alcohol being then determined in the residual oil obtained. The aldehydes may, on the other hand, be transformed into the corresponding alcohols by means of sodium amalgam, the alcohols being determined before and after this action and the content of aldehydes thus deduced. In these cases, however, only approximate results are obtainable, since the separation or transformation of the aldehydes seldom takes place quantitatively.

Acetylation is of special importance with those essential oils, the value of which depends largely on their content of alcoholic principles ; such, for instance, are mint (menthol), palmarosa, geranium, rose (geraniol), coriander, linaloe (linalool) and sandalwood (santalol) oils.

10. Detection and Determination of the Aldehydes

1. Qualitative Tests.—Essential oils containing aldehydes give the following reactions :

(a) When shaken with decolorised fuchsine solution (Schiff's reagent) they give immediately an intense red coloration.

(b) When heated in alcoholic solution with a small quantity of meta-phenylenediamine they yield a brownish-yellow or intense brown coloration.

(c) When shaken with a little concentrated sodium bisulphite solution, oils very rich in aldehydes form a crystalline mass, more or less readily soluble in excess of the bisulphite.

2. Quantitative Determination.—The two following methods are those commonly used :

(a) BISULPHITE METHOD. Into a flask of about 100 c.c. capacity and having a neck about 13 cm. long and 8 mm. in width and graduated in tenths of a cubic centimetre, are poured 10 c.c. of the essential oil and an equal volume of 30% sodium bisulphite solution. The whole is well shaken and heated on a water-bath until the crystalline magma formed begins to sink. The bisulphite solution is then again added, gradually and with shaking, until the flask is about two-thirds filled, the flask being left on the water-bath until solid particles are no longer observed, the aqueous liquid is sharply separated from the supernatant oil, and the characteristic odour of the essential oil cannot be perceived. After cooling, a further quantity of bisulphite is added to bring all the oily portion into the graduated neck of the flask and make the line of separation between the two liquids coincide with the first division of the neck.

From the number of c.c. of oily liquid, which represents the non-aldehydic part of the oil, the quantity of aldehydes (by volume) is calculated by difference.

(b) SULPHITE OR BURGESS' METHOD. Into the flask used in the preceding method are introduced 5 c.c. of the essential oil, 10–20 c.c. of a saturated normal sodium sulphite solution (40%)—freshly-prepared—and a few drops of phenolphthalein solution. The liquid is heated on a water-bath, with frequent shaking and occasional neutralisation of the alkalinity (caused by formation of sodium hydroxide) by means of dilute acetic acid (1 : 5) ; this procedure is continued until fresh addition of sulphite, followed by

heating, causes no further red coloration. Water is then added to bring the unattacked part of the oil into the graduated portion of the neck and the volume of this part read when quite cold.

This method is also used for the determination of *ketones*, such as carvone and pulegone, in caraway and pennyroyal oils.[1]

The determination of aldehydes and ketones is of importance in the analysis of those essential oils characterised especially by aldehydic or ketonic principles, e.g., the citral contained in lemon and lemongrass oils, citronellal in citronella oil and some eucalyptus oils, benzaldehyde in bitter almond oil, salicylaldehyde in meadow-sweet oil, anisaldehyde in aniseed and fennel oils, cuminaldehyde in cumin oil, cinnamaldehyde in cinnamon oil, carvone in caraway oil, pulegone in pennyroyal oil and methyl nonyl ketone in rue oil. The determination of the aldehydes and ketones presents, however, difficulties and the above methods are moderately exact in only a few cases, especially when the content of aldehydes or ketones is considerable. The bisulphite method is applicable particularly to the determination of cinnamaldehyde and benzaldehyde in cinnamon oil and bitter almond oil, and, up to a certain point, to that of citral in lemongrass oil. The sulphite method gives good results in the same cases and for the determination of carvone and pulegone.

11. Determination of the Phenols

The volatile oils which contain phenols, when shaken with caustic soda or potash solution, diminish in volume owing to the ready solubility of the phenols in alkali. Acidification of this alkaline solution results in the separation of the phenol, which is recognisable by its odour and by the greenish-blue or reddish coloration it gives with ferric chloride.

For determining the phenols use is made of a flask, with the neck graduated as with that employed for estimating aldehydes (*see* p. 281). In this, equal volumes (usually 10 c.c.) of the essential oil and of 5% caustic soda solution [2] are shaken vigorously together, a further quantity of the alkali solution being added to bring the unattacked part into the graduated neck of the flask. When the two liquids have become quite separate and clear, the volume occupied by the part of the oil insoluble in the alkali is read off, the volume of the phenol being determined by difference.

Determination of the phenols is of special importance in the analysis of hop (carvacrol), thyme, ajowan (thymol), aniseed, badiana, fennel (anethole), clove bud and stem (eugenol) and sassafras oils (safrole).

12. Special Investigations

The commonest adulterations of essential oils consist in addition of extraneous substances of little value, those most frequently used being :

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[1] Other methods for the determination of aldehydes and ketones are those of Benedikt and Strache (*carbonyl number*), Hanus (phenylhydrazine), and Bennett (hydroxylamine hydrochloride). *See* Charabot, Dupont et Pillet : *Les Huiles essentielles*, 1899.
    The carbonyl number method gives moderately exact results for the determinations of benzaldehyde in bitter almond oil, of cuminaldehyde in cumin oil and of methyl nonyl ketone in rue oil. The method devised by Hanus gives, according to this author, good results for the amount of cinnamaldehyde in cinnamon oil.
[2] With volatile oils containing eugenol (clove bud or stem, cinnamon, pimento or bay oil), 3% sodium hydroxide solution must be employed. With clove stem oil it is well to heat for 10 minutes on a water-bath.

alcohol, mineral oils, fatty oils, oil of turpentine, cedarwood oil, copaiba oil and gurjun balsam oil. Paraffin wax and spermaceti are also used, especially for the adulteration of rose oil.

In special cases genuine oils are adulterated with secondary products from the treatment of certain oils, as, for instance, the terpenes of the lemon for adulterating acid fruit oils (*q.v.*), or oils of high value are treated with others of similar odour but of much lower price (geranium oil being added to rose oil or citronella oil to melissa oil).

In Table XXXIV the most usual adulterations of the essential oils are indicated. The more common adulterants (alcohol, mineral oils, etc.). may, in general, be tested for as follows :

1. Alcohol.—(*A*) QUALITATIVE TEST. Essential oils mixed with alcohol give the following reactions :

(*a*) When a test-tube containing about 2 c.c. of the oil and closed with a plug of cotton-wool in which is placed a granule of fuchsine, is heated in a water-bath, the cotton-wool turns red.

(*b*) A few drops of the oil, shaken up with 5–10 c.c. of water, give a .ilky liquid (pure oils separate rapidly from the water, leaving this clear).

(*c*) If a certain volume (e.g., 10 c.c.) of the oil is shaken in a graduated cylinder with an equal volume of salt water or dilute glycerine (water and glycerine in equal volumes) and then left to stand until the two liquids have completely separated, the volume of the oil will be found to be diminished owing to the alcohol present ; the amount of the latter may be judged approximately. If the aqueous liquid is distilled, ethyl alcohol may be identified in the distillate by the reactions described in the chapter dealing with varnish.

(*B*) QUANTITATIVE DETERMINATION. For a more exact determination, especially with perfumery, the following method may be recommended [1] : To 50 c.c. of the product in a 200 c.c. flask is added, with shaking, 5% alum solution almost up to the mark. The liquid is cooled to 15°, made up to volume with the alum solution, shaken and filtered through a dry filter, the first portions of the filtrate, if turbid, being either rejected or returned to the filter. 100 c.c. of the filtrate are diluted with a little water and distilled, 100 c.c. of distillate being collected ; the specific gravity is then determined and the percentage of alcohol by volume read off from the usual tables ; multiplication by four gives the percentage of alcohol by volume in the oil.

2. Mineral Oils.—Petroleum, heavy mineral oils and paraffin oil may be detected in essential oils owing to their insolubility in 90% alcohol ; they also diminish the specific gravity.

To determine them quantitatively, the essential oil is oxidised completely with fuming nitric acid, as in the estimation of petroleum in oil of turpentine (*see* Chapter IX, this volume). Some ethereal oils, such as rose, chamomile and neroli oils, contain naturally solid hydrocarbons (paraffin wax).

3. Fatty Oils.— Volatile oils mixed with fatty oils leave a transparent, greasy spot when a few drops are evaporated on paper.

[1] D. Marino : *Ann. Labor. chim. centr. Gabelle*, Vol. VI, p. 661.

These mixtures are not completely soluble in 90% alcohol, except in presence of castor oil, which is, however, only slightly soluble in 70% alcohol. When, therefore, they are evaporated in a dish on a water-bath, they leave an abundant residue which has a high saponification number (180–200) and emits an irritating odour of acrolein when heated in a test-tube with potassium bisulphate. Certain ethereal oils (bergamot, lemon, aniseed and badiana oils) themselves leave a residue on evaporation, but such residue has not the characters of the fatty oils. The saponification number of the oil itself may raise suspicion as to the presence of fatty oil.

Fatty oils are used to adulterate bergamot oil, and coconut oil is often added to cananga, citronella and palmarosa oils.

4. Oil of Turpentine.—This is a common adulterant for the volatile oils and is not always easy to detect. In most cases use is made of the specific gravity, fractional distillation and rotatory power, and the characters of oil of turpentine are described in Chapter IX (*see also* Oil of Lemon).

By reason of its slight solubility in 70% alcohol, oil of turpentine may be discovered in those oils which are readily soluble in such alcohol.

In oils which do not number pinene among their components, ordinary oil of turpentine (*see* Chapter IX) may be recognised by identification of the *pinene*. For this purpose the fraction of the oil boiling at about 160° is collected and is treated with a mixture in equal volumes of glacial acetic acid and amyl nitrite in a vessel kept immersed in a mixture of snow and salt ; hydrochloric acid of D = 1·17 (1·5 gram per 5 grams of substance) is then added, little by little and with shaking. In this way *pinene nitrosochloride* is formed in white nacreous scales, which are treated with cold 96% alcohol, pumped off and washed with cold alcohol, pressed between filter-papers and purified by dissolution in a little chloroform and reprecipitation with methyl alcohol (it may also be recrystallised from benzene). Pure pinene nitrosochloride melts at 103° to a liquid which froths and becomes blood-red. When boiled for a moment with alcohol and a little aniline, it gives an intensely yellow solution which turns red on neutralisation with hydrochloric acid. When it is heated for some time on a water-bath with alcohol and an excess of piperidine or benzylamine and then diluted with water, the corresponding characteristic *nitrolamines* separate, *pinene nitrolpiperidine* melting at 118–119° and *pinene nitrolbenzylamine* at 122–123°.

5. Cedarwood Oil, Copaiba Balsam Oil and Gurjun Balsam Oil.—These volatile oils lend themselves readily to the adulteration of many essential oils, owing to their cheapness and slight odour.

They may be detected in mixtures by virtue of their insolubility in 70% or 90% alcohol, their high sp. gr. (above 0·9), their high b.pt. (250–285°) and their high rotatory power (a_D = − 20° to − 40°, − 7° to − 35° and − 35° to − 130° for the oils of cedarwood, copaiba and gurjun balsam respectively ; there is, however, an African copaiba oil with a dextrorotation of + 16° to + 22°).

SPECIAL PART

The number of essential oils which are obtained from flowers, fruits, peel, leaves and secretions of different plants or are prepared synthetically, is very large. Some are, however, of little commercial interest, whilst others are of great importance, especially in certain regions. In the following pages, attention is paid chiefly to the oils of the acid fruits (orange, lemon, etc.), the characters of other oils being dealt with in Table XXXIV.

BITTER ORANGE OIL (Essence d'orange-bigarade)

This is obtained from the peel of *Citrus bigaradia* and is an intensely yellow liquid with an orange odour and an aromatic bitterish taste. It consists of d-limonene with small quantities of citral, methyl methylanthranilate and other components not well identified. Its usual adulterants are orange and lemon terpenes, oil of lemon and oil of turpentine; these are tested for by determining the specific gravity at 15°, by fractional distillation,[1] by measuring the rotation and by examining the residue left on evaporation by the methods given for oil of lemon (*see* later).

<p style="text-align:center">*
* *</p>

The *genuine oil* should have : D $= 0.852-0.857$, a_D at 20° $= + 88°$ to $+ 96°$, b.pt. 175–200°; with 90% alcohol it gives a turbid solution. On fractional distillation by the Soldaini and Berté method (*see* Oil of Lemon) it should give a distillate with rotation (at 20° C.) not less than 3° higher than that of the oil itself. On evaporation it should leave 3–5% of residue, which is usually distinctly red.

SWEET ORANGE OIL (Portuguese)

This is obtained from the peel of the fruit of *Citrus aurantium* (var. *dulcis*) and is a golden-yellow liquid with an odour of oranges and a sweetish, aromatic taste. It contains limonene (about 90%), linalool, terpineol, nonyl alcohol, decyl aldehyde and esterified caprylic acid. If adulterated with bitter orange oil (*q.v.*), the latter is detectable by determinations of the sp. gr. at 15°, rotatory power and residue on evaporation (*see* Oil of Lemon) and by fractional distillation.

As regards the *rotation*, this is more influenced by the temperature than that of oil of lemon (*q.v.*) ; for temperatures, t, above 20°, add $(t - 20) \times 13'$ to the observed rotation and for temperatures below 20° subtract $(20 - t) \times 14'$, to obtain the correct value at 20°.

<p style="text-align:center">*
* *</p>

The *genuine oil* has : D $= 0.847-0.852$; a_D at 20° C. $= + 96°$ to $+ 98°$; b.pt. 176–200°. Owing to the narrow limits of the density and rotation adulteration is easily detected.

On fractional distillation by the Soldaini and Berté method (*see* Oil of Lemon), the rotation should be raised by at least 1° 30′ and the residue on evaporation should be 2–4%.

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[1] The distillate exhibits faint blue fluorescence—which becomes more pronounced on addition of alcohol—owing to the presence of methyl methylanthranilate.

BERGAMOT OIL

This is obtained from the skins of the fruit of *Citrus bergamia* and is a greenish or greenish yellow liquid with a peculiar fragrant odour. It contains : d-limonene, dipentene ; linalyl acetate (33–45%) which is the chief constituent determining its value ; free linalool : an odourless stearoptene, termed bergaptene (about 5%) ; small proportions of fatty, resinous and waxy substances.

The following lower qualities of bergamot oil are also obtained : *Bergamot black* (Nero di bergamotto), from unripe, fallen or bad fruit, is a dark-brown liquid, with a pungent odour less agreeable than that of the normal oil. *Rectified bergamot oil*, prepared by distilling with water the residues from the rasping of the fruit, is a colourless or yellowish liquid with a marked burnt odour.

Bergamot oil is adulterated in various ways, e.g., with oil of turpentine, oil or terpenes of lemon, orange terpenes, fatty oils, waxes, resin, gurjun and Canada balsam, cedarwood oil, mineral oils, chlorinated compounds of oil of turpentine, organic acids, various esters (diethyl succinate, triethyl citrate, diethyl oxalate, terpinyl acetate, esters of oleic, phthalic, tartaric and acetic acids). Such adulteration is usually made judiciously, the genuine oil being treated with such quantities of one or more picked adulterants as will not alter too markedly the characters of the oil itself.[1]

Artificial bergamot oils are also sold, these being composed, for instance, of triacetin, terpenes and a little bergamot oil ; such are either used as they are or are employed as diluents of the pure oil.[2] Bergamot oil is sometimes diluted also with the black or with the rectified oil referred to above.

To decide if a sample of the oil is genuine or otherwise, it is analysed completely as follows :

1. External Characters ; Specific Gravity ; Rotatory Power ; Solubility in 90% and 80% Alcohol.—These determinations are made as described under General Methods.

The liquid being coloured, the rotation must be read in a tube 2 or 2·5 cm. in length, the temperature being 15–20°.

2. Acid and Ester Numbers.—These are determined as indicated on p. 279, the acidity being expressed also as per cent. of acetic acid (acid number $\times$ 0·1071 = % of $C_2H_4O_2$). From the acid number the percentage of linalyl acetate is calculated by the formula, $\dfrac{(\text{ester number}) \times 196}{560}$, this result being then diminished by the percentage of linalyl acetate calculated on the residue left by the oil on evaporation (*see* paragraph 3).

3. Residue on Evaporation.—5 grams of the oil are evaporated in a tared dish on a water-bath until the odour disappears, the residue being then weighed and calculated for 100 grams of the oil.

[1] For instance, addition of oil of turpentine or lemon or orange terpenes—which lower the sp. gr. and the ester content—together with fatty oils, resin, balsams and synthetic esters—which have the opposite effect.

[2] A sample of such products gave : $D = 1·062$, $a_D = +13°$ and saponification number = 555 (Coen : *Ann. Lab. chim. centr. Gabelle*, Vol. VII, p. 89).

Of this residue, dissolved in a little neutral alcohol, the acid and ester numbers are determined, these being due to resinous, fatty and waxy substances naturally present in the bergamot oil. The ester number is converted into the corresponding percentage (n) of linalyl acetate (see paragraph 2) and the quantity of this ester contained in the percentage (r) of residue left by the oil then calculated from the formula, $(n \times r)/100$. This amount of linalyl acetate is subtracted from that found in the oil, as in paragraph 2.

4. Fractional Distillation (*Romeo and Moricca's method*).—30 c.c. of the oil are distilled either under reduced pressure (20–30 mm.) in an oil-bath or at ordinary pressure by direct heating, two fractions of exactly 5 c.c. each being collected. The rotatory power (at 15–20°) of the distilled fractions and of the residue are determined and referred to a tube 10 cm. long.

The mean of the rotations of the two fractions, reduced to minutes, representing the rotation obtainable by distilling one-third of the oil, is divided by the direct rotation of the oil, also reduced to minutes: the quotient gives the *ratio* between the rotation of the oil and that of the product (one-third) of its distillation.

5. Detection of the Aldehydes.—This is effected with Schiff's reagent (General Method, No. 10) on about 2 c.c. of the oil dissolved in pure alcohol: in presence of aldehydes a magenta-red coloration is obtained immediately. Also when 2–3 c.c. of the oil, dissolved in 10–15 c.c. of pure alcohol, are heated with a small quantity of metaphenylenediamine hydrochloride, a yellowish-brown coloration (faint yellowing is allowable) is formed in presence of aldehydes.

6. Detection of Acetins.[1]—10 c.c. of the oil are shaken repeatedly with 40 c.c. of 10% alcohol, in which acetin is readily soluble and the oil practically insoluble; after standing, the aqueous-alcoholic liquid is filtered through a filter moistened with the same alcohol. The oil and filter are washed with other small quantities of 10% alcohol, the alcoholic liquids being then evaporated on the water-bath to a small volume (5–10 c.c.). This residue is taken up in neutral alcohol, neutralised with N/10-potassium hydroxide (with phenolphthalein), and saponified with N/2-potassium hydroxide, in the usual way, the volume of the alkali required for saponification being noted.

After this operation, the liquid is evaporated to dryness and the residue taken up in a mixture of 2 vols. of absolute alcohol and 1 vol. of anhydrous ether. The solution is filtered, the solvent evaporated and the new residue heated with potassium bisulphate: in presence of glycerine (from the saponification of the acetins) an odour of acrolein is emitted and the vapours impart a dark blue colour to a paper steeped in a fresh solution of sodium nitroprusside and piperidine.

7. Detection of Terpinyl Acetate (*Schimmel's method*).—The saponification of the linalyl acetate of bergamot oil is complete after 15–30 minutes' boiling with N/2-alcoholic potash, but with terpinyl acetate at least an hour is necessary for complete saponification. The latter ester may thus be detected by carrying out two distinct saponifications, one for 30 minutes

E. Coen; *Ann. Labor. chim. centr. Gabelle*, Vol. VII, p. 89.

and the other for an hour or rather longer. If the two results either agree or differ by not more than 2, the oil does not contain terpinyl acetate, but if the difference exceeds 2, the presence of this ester is proved (5%, 10% and 25% respectively of terpinyl acetate give differences of about 3·5, 5·5 and 11).

8. Detection of other Esters of Fixed Acids (*oxalates, tartrates, succinates, citrates*).—A certain quantity of the oil (if possible 10–20 c.c. or more) is saponified in the usual way, the excess of alkali being neutralised with hydrochloric acid in presence of phenolphthalein and the alcohol expelled on a water-bath. The residue is diluted with water and extracted with ether, the aqueous solution being tested for oxalic, tartaric, succinic and citric acids by the ordinary analytical methods.

9. Detection of Chlorinated Compounds of Oil of Turpentine.— The oil is saponified with alcoholic potash (free from chlorides), evaporated to dryness and calcined, and the residue tested for chlorides.

<div align="center">*
* *</div>

The characters of genuine bergamot oil are : $D = 0.880-0.887$; $a_D = + 7°$ to $+ 25°$ (usually $+ 10°$ to $+ 20°$) ; b.pt. $= 180°$ and upwards ; saponification number 95–130 ; acid number, up to 3·5 (in oils of good quality the acidity as acetic acid varies from 0·15 to 0·20% ; in old oils it may reach 0·4%, but not more than this) ; content of linalyl acetate $= 33-45\%$, according to the degree of ripeness of the fruit, the season, the district, etc. It is soluble in one-half its volume or more of 90% alcohol, or in 1 vol. of 80% alcohol, but with the latter an opalescent liquid is sometimes obtained.

A bergamot oil which does not correspond with the more important of the above specific characters for the genuine oil is to be regarded as adulterated. This is the case, for instance, with an oil having D below 0·880 or above 0·887 or a_D below $+ 7°$ or above $+ 25°$, or containing less than 33% or more than 45% of esters (as linalyl acetate), or not dissolving completely in half its volume of 90% alcohol.

In view, however, of the limits between which these characters vary and the complexity of the frauds already mentioned, it is evident that a bergamot oil may be adulterated even when it exhibits normal characters. In such cases its purity can be judged only by a complete analysis. The following points require attention :

A very deep *colour*, with high specific gravity, denotes the presence of bergamot black ; a burnt *smell* with a low specific gravity and a low proportion of esters,[1] indicates the rectified oil.

A *specific gravity* below the normal limits denotes the presence of oil of lemon, lemon or orange terpenes, or mineral oils, whereas a higher value than the upper limit shows the presence of fats, balsam or resin.

The *rotatory power* is increased by oil of lemon or by terpenes and diminished by lævo-rotatory oil of turpentine, mineral oils, etc.

Incomplete *solubility* in 90% alcohol indicates the presence of terpenes, oil of turpentine or mineral oil.

Acidity above that indicated for the genuine oil may be due to addition of organic acids.

The *residue on evaporation* of the genuine oil is 5–6% and its ester number 138–180, corresponding with 47·6–63% of linalyl acetate ; the 5–6 grams of residue are thus equivalent to about 2·4–3·8 grams of linalyl acetate. Oil of lemon, terpenes, rectified bergamot oil or mineral oils diminish the residue

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[1] Bergamot black has $D = 0.890-0.896$ and contains 20–35% of linalyl acetate. Rectified bergamot oil has $D =$ about 0·865 and contains 3–6% of linalyl acetate.

on evaporation, while fatty oils, balsams, resin and certain fixed esters increase it and also raise the saponification number.

Fractional distillation: With the genuine oil the second fraction has a lower rotation than the first, while the residue has a positive rotation, the value of which may be $+ 2°$ (or up to $+ 6°$) when the original rotation is not more than $+ 16°$ (or higher than $+ 16°$).

The *ratio* between the original rotation and that of the one-third distillate increases as the original rotation diminishes: it varies between the following limits according as the distillation is carried out at 20–30 mm. or ordinary pressure:

Original Rotation.	Ratio at		Original Rotation.	Ratio at	
	Reduced Pressure.	Ordinary Pressure.		Reduced Pressure.	Ordinary Pressure.
10°	3·4	2·7	16°	2·4	2·0
11	3·2	—	17	2·3	1·8
12	3·0	—	18	2·2	—
13	2·8	2·5	19	2·1	1·7
14	2·6	2·3	20	2·0	—
15	2·5	2·0			

If the rotation of the second fraction exceeds that of the first, the presence of oil of lemon, terpenes or oil of turpentine (if the last is dextro-rotatory it is also detectable when at least 10% is present) is indicated; in such case the residue from the distillation will have a rotation exceeding $+ 2°$ or $+ 6°$, according to the original rotation of the oil.

If the ratio of the original rotation to that of the one-third distillate is less than that indicated in the above table, the presence of lævo-rotatory or slightly dextro-rotatory, or of a marked quantity (not less than 10%) of strongly dextro-rotatory oil of turpentine is indicated.

Positive *reactions for aldehydes* indicate the presence of oil of lemon.

In the test for *acetins* with genuine oils 0·1–0·2 c.c. of N/2-KOH usually suffices to saponify the very small amount of extract from the 10% alcohol; in presence of acetins a somewhat large volume is required. The acrolein test will then indicate if acetins are really present.

OIL OF LEMON

This is extracted from the peel of the fruit of *Citrus limonum* by pressure, either manual or mechanical. It is a pale yellow, sometimes slightly greenish liquid with the smell of fresh lemons; in time it resinifies, decolorises and acquires a special resinous odour. It consists mostly (about 90%) of limonene and contains also small proportions of other terpenes, citral (which determines its value, as it contributes largely to the aroma) and other aldehydes and traces of esters.

The usual adulteration is with oil of turpentine, sometimes in conjunction with a little orange oil or with lemon or orange terpenes; paraffin oil, fatty oils and balsams are rarely used. These adulterants are detected and the value of the oil determined by the following tests:

1. External Properties. Specific Gravity. Solubility in Alcohol.
—*See* General Methods.

2. Rotation.—Measured on the original oil and on the products of its distillation.

(*A*) ORIGINAL OIL. The procedure is as described in General Methods. The rotation is, however, affected by temperature, and readings are usually made at 20° C. ; each degree below 20° increases the reading by 9 minutes, while each degree above 20° diminishes it by 8 minutes.

(*B*) DISTILLATION PRODUCTS. The two following methods are equally good and both should be applied in cases of doubt.

1. *Soldaini and Berté's method.* 20 c.c. of the oil and a few scraps of pumice are placed in a three-bulbed distillation flask (*see* p. 278) holding about 70–75 c.c., the flask being connected with a small condenser and closed with a cork traversed by a thermometer. Around the flask—which should rest on an asbestos-gauze—is placed an asbestos card sleeve, which surrounds it at a distance of about 1 cm. and reaches almost to the lowest bulb of the neck. To the free end of the condenser is fitted a graduated cylinder. The oil is then boiled at the ordinary pressure so that one drop falls into the cylinder about every two seconds. When the *distillate* in the cylinder amounts to one-half the amount of oil taken, i.e. 10 c.c., the cylinder is replaced by an ordinary test-tube and the flame extinguished. The few drops of subsequent distillate are returned to the *residue* in the distillation flask.

The distillate—usually turbid owing to the presence of a little water—is shaken with a small quantity of anhydrous sodium sulphate, filtered and polarised in a 10 cm. tube, note being made of the temperature ; the reading is corrected to 20° C. (*see A*, above). Comparison of this rotation with that of the original oil (*see A*, above) indicates if the oil is genuine or mixed with oil of turpentine or lemon terpenes (*see* below).

2. *Schimmel's method.* The procedure is as in (1), 50 c.c. being distilled from a flask holding about 100 c.c. and the first one-tenth, i.e., 5 c.c., collected. The distillate, shaken with a little anhydrous sodium sulphate and filtered, is polarised in a 2 cm. tube, the reading being multiplied by 5 and referred to 20° C.

3. Residue on Evaporation.—5 grams of the oil are evaporated in a dish on a water-bath until distinct odour disappears, the residue being weighed when cold and then reheated for half an hour and reweighed.

4. Determination of the Citral.—Use is commonly made of *Berté's method,* based on the change of rotation due to removal of the aldehydes by means of alkali bisulphite.

10 c.c. of the oil and 50 c.c. of saturated potassium bisulphite solution are placed in a conical flask holding about 250 c.c., the flask being closed by a stopper carrying a glass tube about 45 cm. long and well shaken to emulsify the two liquids. It is then placed on a water-bath for 10 minutes, being well shaken meanwhile and care being taken that the liquid does not become heated too much. It is next allowed to cool completely, placed on the water-bath for 5 minutes and vigorously shaken meanwhile and then cool to the surrounding temperature. The liquid is then placed in

a 100 c.c. separating funnel and left until the part of the oil unacted on by the bisulphite collects in a clear, surface layer. After removal of the aqueous liquid, the oil is shaken with a little anhydrous sodium sulphate, filtered and polarised in a 10 cm. tube at the *same temperature* as the original oil. From the difference between the two rotations, the percentage (by volume), C, of aldehydes is calculated by means of the following formula :

$$C = \frac{100 \ (A - \alpha)}{A},$$

where α is the original rotation and A that of the aldehyde-free oil.

Besides this method, which is simple and rapid and, if not highly exact, gives comparable results, there are others,[1] but these are not free from inconveniences and also not exact.

5. Detection of Orange Oil.—1 or 2 drops of the oil are treated with 15–20 drops of a 5% solution of bromine in chloroform : pure oil of lemon gives a colourless liquid, whilst a yellow liquid is obtained in presence of orange oil.

When treated with bisulphite, as in the determination of the aldehydes, the pure oil exhibits no coloration, whereas a yellow precipitate forms in presence of oil of orange.

<p style="text-align:center">**
* *</p>

The *characters* of *genuine* oil of lemon and the *deductions* to be drawn from the results obtained are as follows :

External characters. The genuine oil has normal colour and smell. Large additions of terpenes weaken the colour; oil extracted mechanically is more coloured than that pressed by hand.

Specific gravity. For the genuine oil, $D = 0.855$–0.861 ; for hand-pressed oil the value is slightly lower than for that pressed by machinery. Terpenes lower the sp. gr., whilst fatty oils and balsams raise it.

Boiling point. The genuine oil boils at about 173–220°, the bulk distilling at 174–178°.

Solubility in alcohol. The genuine oil dissolves in 5 vols. of 90% alcohol, sometimes giving an opalescent liquid ; it is not completely soluble in more dilute alcohol.

Rotatory power. The rotation has a value between $+ 55°$ and $+ 67°$, according to the origin of the fruit, their degree of maturity, the season and other causes. The lower rotations (about 56° or even less) are given by oil from poorly developed, over-ripe or altered fruit and by oil which has been stored badly.

The high rotations are given mostly by oils from Syracuse or Barcellona (Messina).

Oil of turpentine lowers the rotation, but the latter alone is insufficient for the detection of such an addition, since the value for the genuine oil may vary so widely, and that for oil of turpentine may have any magnitude between $- 40°$ and about $+ 80°$ (10 cm. length), while any alteration thus produced in the rotation may be neutralised by addition of oil of orange ($\alpha_D = + 96°$ to $+ 98°$). More reliable results may be obtained by association of this determination with fractional distillation, the first fractions containing a preponderance of the oil of turpentine, which has a slightly lower boiling point than oil of lemon.

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[1] Other methods of determining citral (aldehydes) are that of Soldaini and Berté and that of Romeo (*Ann. Lab. Camera di Commercio di Messina*, 1908). Results obtained by Kleber's phenylhydrazine method or Walther and Bennet's hydroxylamine method are sometimes required in the trade ; the latter gives lower results than other methods.

Characters and Compositions of

Essential Oil of	Sp. gr. at 15°.	Solidifying Point (° C.).	Rotation in 10 cm. Tube.	Refractive Index, n_D.	B.pt. (° C.).	Alcohol required to dissolve 1 Vol. of Oil.		
						70%. Vols.	80%. Vols.	90%. Vols.
Almond (bitter) . . .	1·045–1·070	—	0	1·5500 (12°) / 1·5420 ⟩ (15°) / 1·5463	178–180	1·5–2	—	Very sol.
Aniseed	0·980–0·990 (at 20°)	15–20	− 1 to − 2	1·5566 (10°)	209–230	—	—	2–3
Badiane (*see* Star Anise)								
Birch (bark and twigs) .	1·180–1·187	—	0	—	217–221	5–8	—	—
Cajuput	0·920–0·930	—	0–2	1·4611 (25°) / 1·4680 (15°)	175–252	3–5	1	—
Cananga	0·910–0·940	—	− 17 to − 55	—	—	—	—	slightly sol.
Caraway	0·907–0·915	—	+ 70 to + 80	1·4638 (15°)	175–245	—	3–10	1
Cassia (Ceylon) . . .	1·023–1·040	—	− 1	1·5353 ⟩ (15°) / 1·6000	220–241	3	—	—
Do. do. (leaves) .	1·044–1·065	—	− 1	—	—	3	—	—
Do. (Chinese) . . .	1·055–1·070	—	− 1 to + 6	1·5800 ⟩ (15°) / 1·6016	240–260	3–4	1–2	—
Cedarwood (Juniperus virginiana L.)	0·945–960	—	− 20 to − 40	1·5050 (12°) / 1·5300 (15°)	271–285	—	—	10–20
Chamomile (ordinary) .	0·930–0·945	0	0	1·4620 (12°) / 1·5110 ⟩ (15°) / 1·4710	105–300	—	—	8
Do. (Roman) . .	0·905–0·915	—	+ 1 to + 3	—	147–250	6	—	—
Cherry laurel (leaves) .	1·054–1·066	—	0	—	—	2	—	—
Citronella (Andropogon nardus L.)	0·886–0·920	—	0 to − 21	1·4659 (21°)	200–240	—	1–2	—
Clove (buds)	1·044–1·070	—	± 1	1·5420 (12°) / 1·5290 (15°) / 1·5312 (17°)	250–260	2	—	—
Do. (stems) . . .	1·040–1·065	—	± 1	—	—	2	—	—
Copaiba	0·900–0·910	—	− 7 to − 35	1·5045 (15°)	250–275	Insol.	Insol.	Diffic. sol.
Do. (African) . .	0·917–0·918	—	+ 16 to + 22	—	—	Insol.	Insol.	Insol.
Coriander.	0·870–0·890	—	+ 8 to + 13	1·4652 (10°)	150–200	3	—	—
Cubeb.	0·910–0·930	—	− 25 to − 40	1·5011 (10°) / 1·4970 (16°)	175–300	—	—	1–10
Cumin.	0·90–0·97	—	+ 4 to + 8	1·4903 (10°) / 1·4930 (12°)	180–230	—	3	—
Estragon or Tarragon (Artemisia dracunculus L.)	0·900–0·960	—	+ 2 to + 9	—	200–206	—	10	—
Eucalyptus (E. globulus)	0·910–0·930	—	+ 1 to + 15	—	170–190	3	—	—

the Commoner Essential Oils

Saponification Number.	Principal Components of the Oil.	More Common Adulterants.
—	Benzaldehyde, hydrocyanic acid (1·5–4%), phenoxyacetonitrile	Artificial benzaldehyde, nitrobenzene
—	Anethole (80–90%), methylchavicole, terpenes . .	Oil of fennel, anise terpenes, spermaceti, fatty oils, oil of turpentine. Chief tests : solidifying pt., solubility in alcohol
—	Methyl salicylate (98–99%), esters, paraffin . . .	Mineral oils, oil of turpentine
—	Cineol, terpineol, pinene, valeraldehyde, benzaldehyde (small amount)	Oil of turpentine, oil of rosemary, essence of camphor ; may contain traces of Cu
10–30	Same as ylang-ylang oil	Coconut oil
—	Carvone (50–60%), d-limonene.	Oil of turpentine, caraway terpenes
—	Cinnamaldehyde (65–76%), eugenol (4–10%), pinene, phellandrene, cimene, caryophyllene, linalool	Oil of cassia leaves, Chinese cassia oil, Chief tests : estimation of aldehydes and eugenol
—	Eugenol (70–90%), cinnamaldehyde (less than 1%), hydrocarbons	—
—	Cinnamaldehyde (75–90%), cinnamyl acetate, hydrocarbons	Cedarwood or gurjun oil, mineral oil, colophony, fatty oils ; may contain traces of Pb
—	Cedar camphor, hydrocarbons	—
About 45	Terpenes, caproic esters, blue oil (azulene and cerulein)	Cedarwood oil, oil of turpentine.
250–300	Isobutyl, amyl and hexyl butyrates, angelates and tiglates, paraffin (anthemene), camphor (anthemol)	Do.
—	Benzaldehyde, hydrocyanic acid (3%), traces of phenoxyacetonitrile and benzyl alcohol	Artificial benzaldehyde, nitrobenzene
—	Geraniol and citronellal (50–80%), terpenes, methylheptenone, borneol	Mineral oils, fatty oils
—	Eugenol (80–90%), acetyleugenol (2–3%), caryophyllene, furfural, methyl amyl ketone, salicylic acid (small quantity)	Clove stem oil, cedarwood, copaiba or gurjun oil, phenol, oil of turpentine. Chief test : estimation of eugenol
—	Eugenol (85–95%), no acetyleugenol	—
—	Sesquiterpenes (caryophyllene).	—
—	—	—
—	Linalool, pinene	Oil of turpentine, oil of orange
—	Pinene or camphene, dipentene ; sesquiterpenes, cubeb camphor	—
—	Cuminaldehyde (70%), cymene (23%), terpenes. .	—
—	Methylchavicole, hydrocarbons	—
—	Cineol (55–80%), pinene, terpineol, valer-, butyr- and capraldehydes, esters	Oil of E. amygdalina (lævo-rotatory and consisting of phellandrene)

Table XXXIV

Essential Oil of	Sp. gr. at 15°.	Solidifying Point (° C.).	Rotation in 10 cm. Tube.	Refractive Index, n_D.	B.pt. (° C.).	Alcohol required to dissolve 1 Vol. of Oil.		
						70%. Vols.	80%. Vols.	90%. Vols.
Fennel	0·965 0·977	3–6	+ 12 to + 24	1·4834 (12°) 1·5485 (15°)	190–225	—	6–8	1
Gaultheria	1·180–1·187	—	0 to — 1	—	218–221	6	—	—
Geranium (Pelargonium spec.)	0·890–0·907	—	— 6 to — 16	—	216–222	2–3	—	—
Guaiacum (wood)	0·965–0·975 (38°)	30–50	— 7 (30°)	—	—	1	—	—
Gurjun balsam	0·915–0·930	—	—35 to —130	—	255–256	Insol.	Insol.	Insol.
Juniper (berries)	0·860–0·885	—	— 11 to — 19	1·4793 (15°)	150–300	—	—	8–10
Lavender (English)	0·885–0·900	—	— 1 to — 10	—	200	3	—	—
Do. (French)	0·885–0·895	—	— 3 to — 9	1·4670 (12°) 1·4648 (20°)	200	3	—	—
Lemongrass (Andropogon citratus D.C.)	0·895–0·905	—	— 3 to + 1	1·4705 (24°)	200–222	2	—	—
Limetta (acid), distilled	0·856–0·868	—	+ 38 to + 47	—	—	—	—	4–5
Do. do. pressed	0·87–0·90	—	+ 35 to + 40	—	—	—	—	4–5
Limetta, sweet (Italian) (skins)	0·87–0·89	—	+ 56 to + 60	—	170–200	—	—	—
Linaloe	0·870–0·895	—	— 3 to — 20	—	200	2–3	—	—
Mandarin (peel)	0·854–0·858	—	+ 67 to + 73	—	175–180	—	—	—
Marjoram	0·890–0·910	—	+ 5 to + 22	—	163	—	2	—
Meadowsweet	Above 1	—	—	—	195–200	—	—	—
Melissa	0·894–0·924	—	0 to + 0·3	—	—	—	—	—
Mustard	1·014–1·025	—	0	—	147–153	10	—	Solub.
Neroli (bitter orange) flower	0·870–0·880	—	0 to + 8	1·4676 (18°)	173–180	—	1–2	—
Origanum (Crete or Smyrna)	0·915–0·945	—	— 3 to — 13	—	—	3	—	—
Do. (Trieste)	0·940–0·980	—	± 1	—	—	3	—	—
Palmarosa (Andropogon schoenanthus L.)	0·888–0·900	—	± 2	1·4753 (15°) 1·4714 (21°)	—	3	—	—
Patchouli	0·950–1·000	—	— 40 to — 68	1·5050 (21°)	280–300	—	—	1
Pelargonium (see Geranium)	—	—	—	—	—	—	—	—
Pennyroyal	0·930–0·960	—	+ 17 to + 23	—	180–230	2	—	—
Peppermint, American and English (Mitcham)	0·900 0·920	— 8 to — 20	— 18 to — 35	—	195–250	2–5	—	0·5

Saponification Number.	Principal Components of the Oil.	More Common Adulterants.
	Anethole (50–70%), fenchone, pinene, limonene, phellandrene, dipentene	Oil of turpentine, fennel distillate
	Methyl salicylate (99%), paraffins, aldehydes (traces)	Artificial methyl salicylate
45–100	Geraniol (15–40%); geranyl tiglate (10–42%); citronellol (30–40%), linalool (total alcohols 65–80%); tiglic, valeric, butyric and acetic acids (esterified)	Oil of turpentine, cedarwood oil, fatty oils
4	Guaiol (sesquiterpene hydrate)	
—	Sesquiterpenes	
3–16	Pinene (35%), cadinene, esters, juniper camphor .	Oil of turpentine
14–29	Linalyl acetate (5–10%), cineol (much)	Oil of turpentine, cedarwood oil, ethyl succinate and oxalate
86–158	Linalyl acetate (30–55%), butyric, propionic and valeric (little) esters, linalool, pinene and cineol (trace)	Do.
	Citral (70–85%), methylheptenone (1–3%), geraniol, terpenes	Oil of turpentine, mineral and fatty oils
About 6	Limonene and terpenes, little citral (res. on evap. 3%)	—
About 36	Limonene, citral, esters (res. on evap. 18%). . .	—
75	d-Limonene, linalyl acetate (26%), linalool, limettin	
1–25	Linalool, geraniol, methylheptenone, sesquiterpenes (3%)	Fatty oils
—	d-Limonene, citral (1%), methyl methylanthranilate, alcohols	Oil of turpentine, oil of lemons and oil of orange
10–30	Terpenes, terpineol, borneol, camphor (?) . . .	Oil of turpentine, mineral oils, oil of lemon, thyme oil, spirit
	Salicylaldehyde, methyl salicylate, terpenes, camphor	—
	Citral, citronellal	Substituted by citronella oil or by oil of lemon distilled over melissa
	Allyl isothiocyanate (above 90%)	Carbon bisulphide, petroleum, spirit
24–55	Limonene (80–90%), linalool, linalyl acetate (8–18%), geraniol, methyl anthranilate, paraffin	Oil of acid fruits and petit-grain, spirit, fatty oils, paraffin
	Carvacrol (25–60%), other phenols, linalool, cymol, terpenes	Oil of turpentine
—	Carvacrol (60–85%), cymol, terpenes	Do.
20–40	Geraniol (total, 76–93%; esterified, 5–11%), terpenes, methylheptenone	Oil of turpentine, mineral oils, coconut oil, cedarwood oil, gurjun balsam oil
—	Cadinene, alcohol or camphor (?), blue oil (azulene or coerulein)	Cedarwood oil, cubeb oil, distillate from patchouli
—	Pulegone (80%)	Oil of turpentine
10–40	Menthol (total 40–70%; as acetic and isovaleric esters, 3–15%), menthone (about 9–12%), acetaldehyde, isovaleraldehyde (traces), acetic and isovaleric (trace) acids, pinene, limonene, phellandrene, cadinene, cineol, dimethyl sulphide (trace)	Oil of turpentine, oil free from menthol, oils of other species of mentha

TABLE XXXIV

Essential Oil of	Sp. gr. at 15°.	Solidifying Point (° C.).	Rotation in 10 cm. Tube.	Refractive Index, n_D	B.pt (° C.)	Alcohol required to dissolve 1 Vol. of Oil.		
						70% Vols.	80% Vols.	90% Vols.
Peppermint, green or common	0·910 0·930		laevo	1·4840 (15°)				
Do., Italian	0·908 0·925		-2 to -18	1·467 1·468	195 222			
Do., Japanese	0·895 0·900 (24°)	17-18	30 to -42			5		
Petit-grain	0·885 0·900		2 to +4	1·4600 (21°)			2	
Pine (needles and twigs)	0·870 0·888		-20 to -60		160-200			5
Pinus sylvestris (German and Swedish) (leaves and branches)	0·872 0·890		+7 to +11 Scotch / -7 to -20		160-200			10
Rose (Bulgarian or Turkish)	0·840 0·862 (at 30°)	18-24	-1 to -3	1·4423 (15°) 1·4675	2			Diffic. solub.
Do. (French)	0·822 0·840 (30°)	28	-6 to -8					Diffic. solub.
Rosemary	0·900 0·920		1 to 15	1·4750 (11°) 1·4688 (66°)	150-160		9-10	0·5
Rue	0·833-0·870	8-10	0 to +2		170-250	2-3		
Sandalwood (Santalum album L.)	0·974-0·985		-16 to -21	1·5076 (15°) 1·5100	275-293	5		
Do. (Australian) (S. cygnorum Miq.)	0·953-0·965	Semi-solid	+5					
Do. (West Indian) (Amyris spec. ?)	0·960-0·970		+24 to +30					
Sassafras (wood)	1·060-1·090		+3 to +4	1·5410 (11°)	230-235			1
Spearmint (Menta crispa)	0·920-0·980		-36 to -48		200-210			1-2
Spike	0·905 0·915		+3 to +7		166-186	2-3		
Star anise	0·970-0·990 (20°)	14-18	±2	1·5430 15° 1·5500				1
Thuja occidentalis L. (leaves and twigs)	0·915-0·935		-5 to -15		160-250	3-4		
Thyme	0·900-0·935		Slightly laevo-rot.	1·4755 15° 1·4963	170-180		1-2	0·5
Verbena (Lippia citriodora Kth.)	0·900-0·919		-12 to -16		200-225			1-5
Vetiver (Andropogon muricatus Retz)	1·015-1·030		+25 to +36		210-240		1·5-3	
Wormwood	0·901-0·955		-	1·4935 15° 1·4960	180-210		1-2	
Ylang-Ylang	0·930-0·950		-38 to -43					2

Saponification Number.	Principal Components of the Oil.	More Common Adulterants.
—	—	—
30–45	Menthol (total, 44–59%; esterified, 6–10%) . .	As with the American oil
9–17	Menthol (total, 70–91%; esterified, 3–6%) . . .	Do.
110–245	Linalyl acetate (38–85%), linalool, geraniol, sesquiterpene.	Oil of turpentine, oil of lemon, oil of orange
12–32	l-Pinene, l-limonene, cadinene, phellandrene, sesquiterpenes, bornyl acetate (4–11%)	Oil of turpentine, petroleum
9–12	Pinene, sylvestrene, cadinene, bornyl acetate . .	Oil of turpentine
8–19	Geraniol, citronellol, linalool (total alcohols about 66–75%), geranyl acetate (about 3%), solid hydrocarbons and stearoptene (10–20%)	Geranium oil, sandalwood oil, guaiacum oil, fatty oils, spermaceti, paraffin wax. Chief tests : solidifying pt., saponification number, estimations of total alcohols and stearoptene
7–8	Geraniol, etc., hydrocarbons (26–35%)	Do.
12–20	Borneol (16–19%), bornyl acetate (?) (5–6%), camphor, cineol, pinene, camphene	Oil of turpentine, oil of camphor, mineral oils
3–6	Methyl nonyl ketone (90%), esters, aldehydes . .	Oil of turpentine, mineral oils
5–15	Santalol (90–98%)	Cedarwood, gurjun balsam, copaiba and castor oils
—	Santalol (75%)	—
—	—	—
—	Safrole (80%), pinene, phellandrene (10%), camphor (7%), eugenol (0·5%), sesquiterpenes	Oil of camphor
—	Carvone (56%), terpenes, linalool	Cedarwood oil, gurjun balsam oil
15	Pinene, camphene, cymene, borneol, esters (small) .	Oil of turpentine, rosemary oil
—	Anethole (80–90%), terpenes, methylchavicol . .	As with aniseed oil
—	Borneol and its esters ; thujone, fenchone, pinene .	—
—	Thymol (20–35, rarely 42%), carvacrol (little), cymene, pinene (trace), borneol, linalool, camphor, citral	Oil of turpentine, alcohol, mineral oils, oil free from thymol
—	Citral (20–35%), terpenes, alcohols, esters . . .	Citronella oil and spirit
60–80	Esters, sesquiterpenes	Sandalwood oil, fatty oils
15–110	Thujone (absinthol), thujyl alcohol and its esters (acetic, isovaleric, palmitic), phellandrene, cadinene, blue oil (azulene)	Oil of turpentine
75–120	Linalool and geraniol and their esters, methyl ether of cresol, pinene, cadinene, eugenol, ketones	Coconut oil, champaca oil

Rotation of distillates. When distilled by *Soldaini and Berté's process*, the genuine oil gives a distillate with a higher (about $0 \cdot 1-2°$) or at least unchanged (rarely) rotation [1] and a residue with a lower rotation.

In presence of lævo-rotatory or slightly dextro-rotatory oil of turpentine, even in small quantity ($2-5\%$), the distillate has a rotation below that of the oil. Strongly dextro-rotatory oil of turpentine or lemon terpenes produce a similar effect, if not less than 15% is present.

The residue of the distillation has a higher rotation than the oil when marked quantities of orange oil are present.

When distilled according to *Schimmel's method*, the genuine oil yields a distillate (one-tenth of the oil) with a rotation lower, and a residue with a rotation higher, than that of the oil; in the first case the difference is mostly $1-4°$ and rarely $4.3°$; only with oil from undergrown lemons does it reach $5-6°$.

In presence of lævo-rotatory oil of turpentine (even less than 5%) or dextro-rotatory oil of turpentine (above 5% or 10%, according to the magnitude of the rotation) or terpenes (not less than 15%), the difference between the rotation of the oil and that of the first one-tenth distilled exceeds $4°$.

Residue on evaporation. Genuine oil obtained by the sponge process by hand leaves $2-3\cdot5\%$ of residue, while that obtained mechanically may leave 5%. When the latter is distilled by the Soldaini and Berté method, the rotation of the distillate is usually about $2°$ above that of the original oil.

Fatty oils, waxes, paraffin oil and balsams increase the residue.

Content of citral. The Berté method gives about $6-7\cdot5\%$ (by vol.) of total aldehydes in the genuine oil.

In *conclusion*, when any of the characters of an oil of lemon lies outside the values given for the genuine oils, the product is certainly adulterated, but normal values are no guarantee of purity. The whole of the results must be considered before any reliable judgment is attained.

Other Essential Oils

The commonest essential oils, other than those of the acid fruits, are considered in Table XXXIV, which indicates the most important physical and chemical properties, determined by the general methods, and also the principal components and the more probable adulterants.

In general, when the various characters of an oil lie outside the limits at present admitted (*see* Table XXXIV), it is certain that the oil is not genuine, and when the characters lie very near to the limiting values fraud may be suspected and should be tested for specially.

When the characters are normal, the oil may be regarded as genuine. Sometimes, however, adulteration is carried out so cleverly, by mixing the different adulterants in certain definite proportions, that the characters of the oil are not altered (*see* Oil of Lemon and Bergamot Oil); in such cases, special tests are necessary for the detection of the adulteration.

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[1] Oil from under-developed fruit may give a distillate with a *slightly* lower rotation.
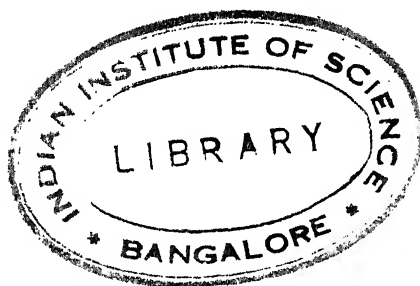
CHAPTER IX

TURPENTINE AND ITS PRODUCTS

Turpentine is an oleo-resin exuded from the trunks of certain conifers (so-called Scio turpentine is obtained from one of the Terebinthaceæ, Pistacia terebinthus L.) and consists essentially of resin acids, neutral resins, volatile oil and small proportions of various other substances (succinic acid, bitter principles, colouring matters, water). Distillation of turpentine and rectification of the distillate gives *oil of turpentine*, the residue being *colophony*. By dry distillation of the latter *resin oils* are obtained. The present chapter deals with the natural product, i.e. turpentine, and with the products obtained from it.

TURPENTINE

The following varieties of turpentine are distinguished.

(*a*) *Pine or ordinary turpentine*, from Pinus pinaster Sol., Pinus sylvestris L., Pinus laricio Poir. (*French* or *Bordeaux turpentine*), Pinus toeda L., and Pinus australis Mich. (*American turpentine*). It is a more or less thick, granular, turbid paste, of a dirty white or yellowish colour and a peculiar and intense odour. On standing it separates into two layers, the upper amber-coloured and semi-fluid and the lower dense and pasty; under the microscope it exhibits crystalline structure, in the air it dries easily, and it is soluble in 96% alcohol (excepting extraneous impurities) but not completely so in 3 parts of cold 85·5% alcohol.

(*b*) *Larch or Venetian turpentine*, called also *pine turpentine*, from Larix europea D. C., is semi-liquid, translucent, viscous, yellowish or greenish and with a peculiar aromatic odour; it has very slight drying properties and dissolves readily in 96% alcohol or in 3 parts of cold 85·5% alcohol.

Besides these genuine, natural turpentines, artificial products (*Turpentine substitutes, Artificial turpentines*) are also sold, these having as their basis, colophony, resin oils, fatty oils, oil of turpentine, pine oil, or resin spirit. Such products have the external appearance of ordinary or larch turpentine, but their odour never possesses the peculiar balsam-like quality characteristic of the latter.

Turpentine is usually analysed with a view to the determination of its commercial value with reference to its purity or its yield of oil, or to estbalish the quality, or to ascertain if it is an artificial product.

The principal tests and determinations are as follows:

1. Impurities or Extraneous Solid Substances.—About 100 grams of the turpentine are dissolved in as much oil of turpentine by gently heating on a water-bath, the solution being then filtered through a tared filter and

299

the insoluble substances washed with oil of turpentine, dried and weighed.

2. Water.—The filtrate from the preceding operation is left to stand in a graduated cylinder and the water separating at the bottom measured.

3. Oil of Turpentine.—100 grams of the turpentine are fractionally distilled, the distillate passing over below 250° being collected and weighed.

The distillation may be carried out in a current of steam and is then continued until no oily drops are condensed with the water ; the volume of the oil separating above the water in a graduated cylinder is then measured : (volume of oil) × (its density) = weight of oil.

4. Acid, Saponification and Ester Numbers.—These are determined as in fatty substances (*see* Vol. I, pp. 374 *et seq.*).

In determining the acid number, the neutral point may be more exactly fixed by adding excess of standard alkali to a solution of the turpentine in neutral alkali and then estimating the excess by titration with acid.

5. Distinction between Larch and Ordinary Pine Turpentine.—The characters given on p. 299 are sufficient to distinguish Venetian from ordinary turpentine, while the acid numbers also differ somewhat in the two cases (*see* below).

It is not, however, easy to ascertain if a larch turpentine contains ordinary turpentine, but some indication in this direction is obtained by *Walbrun's test* : 10 grams of the substance and 30 grams of ether are shaken in a separating cylinder with a ground stopper and the solution then brought to the temperature 20·5° C., which is maintained throughout the test. The liquid is then shaken with 8 c.c. of N/10-ammonia : with pure Venetian turpentine, the whole mass gelatinises in the course of 11 minutes, whereas with the mixed turpentines gelatinisation is complete only after a longer time (more than 20 minutes when 10% of ordinary turpentine is present).

6. Distinction of Artificial from Natural Turpentine.—As already mentioned, artificial turpentines are prepared from colophony (usually 60–70%), resin oil, sometimes fatty oil (castor), and oil of turpentine (5–10%), pine oil or resin spirit (pinolin), and have an odour distinctly different from that of the natural products.

To ascertain if a turpentine is artificial, the products of distillation up to 250° or of steam distillation (*see* paragraph 3) are determined and then examined as described later for oil of turpentine ; the acid and saponification numbers are determined (for the limits, *see* below), and the following tests also made :

(*a*) RESIN OIL. 5 grams of the turpentine are dissolved in 20 c.c. of 96% alcohol, a few drops of alcoholic phenolphthalein being added and then, gradually, 10% aqueous caustic potash solution until a red colour appears : when resin oil is present, a turbid liquid is obtained from which the resin oil is deposited in oily drops.

(*b*) FATS. The turpentine is evaporated in a dish on a water-bath until the smell of the oil is no longer perceptible and is then boiled in a test-tube : in presence of fat, an odour of acrolein is observed, and a rod dipped in concentrated sodium nitroprusside solution containing a little piperidine turns deep blue when brought to the mouth of the tube. The presence of fats may be confirmed by the saponification and ester numbers.

(c) ALCOHOL TEST. 1 gram of the turpentine is shaken in a test-tube with 3 grams of 85·5% alcohol and heated on a water-bath : complete solution indicates natural turpentine, whereas incomplete solution or a turbid liquid shows that artificial turpentine is present to the extent of at least 10%.

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Crude turpentine may contain small quantities (usually not more than 2%) of *extraneous substances*, such as soil, sand, fragments of bark and the like. In some cases clay is added fraudulently.

Good turpentine generally contains only small quantities of *water* (less than 2%), but sometimes as much as 10% is added fraudulently.

The content of *oil* may vary from 15 to 33%, the usual proportions being 20–25% for ordinary turpentine and 15–22% for Venetian.

In general the *acid number* varies between 64 and 165 and the *saponification number* between 87 and 180 ; the *ester number* depends, of course, on the difference between these two. With *ordinary or pine turpentine*, the acid number mostly lies within the limits 100–165 (usually about 120) and the saponification number within the limits 108–180 (usually about 120), the ester number being low. With *larch turpentine* and the like (fine turpentines), the acid number lies mostly within the limits 64–101 (usually about 85) and the saponification number within the limits 87–179 (usually about 140). *Artificial turpentines* have the acid number about 105–120 and a slightly higher saponification number, except when fats are present.

OIL OF TURPENTINE

This is the product of the distillation of natural turpentine, and, after rectification, consists of a clear, colourless liquid with a characteristic odour ; it is insoluble in water, but soluble in alcohol, ether, benzene or petroleum ether. Under the action of air and light, it gradually turns yellow and resinifies.

It may be adulterated with mineral oils, pinewood oil, resin spirit (pinolin), light tar oils (benzene and its homologues), carbon tetrachloride and other chlorinated hydrocarbons. *Substitutes for oil of turpentine* are sold under various names (*Patent oil, Patent turpentine, Terpol, Dapentin, Larixolin, Maikol, Sangajol*). These are mostly composed of those fractions of mineral oils (American, Russian, Roumanian, Galician, Borneo) with D = 0·750–0·820 and b.pt. 140–190°, often together with tar oils, pine oil, camphor oil, mirbane oil, terpinol or oil of turpentine. Pinewood oil, either alone or mixed with a little oil of turpentine is also a very common substitute. So-called *recovered oil of turpentine*, a secondary product of the manufacture of artificial camphor, is a yellowish liquid, b.pt. about 165–175°, with an odour like that of turpentine.

The analysis includes the following determinations.

1. **External Characters.**—The colour, clearness and smell are noted. A yellowish colour indicates a poorly rectified or old or adulterated product (especially one containing crude pine oil). Turbidity or opalescence indicates the presence of suspended impurities, particularly water. The smell, which is well observed by rubbing a little of the oil between the hands, may indicate the presence of mineral or tar oils, etc.

2. Specific Gravity.—Determined at 15° [1] by the ordinary methods.

3. Boiling Point.—This is determined with a distillation flask similar to that used for mineral oils (*see* Vol. I), with a condenser ; 100 c.c. of the oil are distilled and the different fractions—e.g., with b.pts. up to 163°, 163–170°, etc.—collected and measured.

4. Refractive Index.—As with essential oils at 15°.[2] Use may be made of the butyro-refractometer (*see* p. 36), the results being expressed as degrees on this instrument at 15°.

5. Flash Point.—With the Abel apparatus as for paraffin oil (Vol. I, p. 343).

6. Rotatory Power.—In an ordinary yellow light polarimeter in a 10 cm. tube.

7. Residue on Evaporation.—10 c.c. are evaporated in a tared dish on a water-bath. Any weighable residue may be due to old oil (resinified) or to the presence of heavy resin oils or resin.

8. Acidity.—From 5 to 10 grams of the oil are dissolved in neutral alcohol and the acidity measured with N/10-alkali in presence of phenolphthalein.

9. Residue on Polymerisation.—This residue consists of the portion of the oil remaining unattacked (non-polymerised) by concentrated sulphuric acid and is determined in the following manner. In a graduated Babcock vessel 20 c.c. of pure concentrated sulphuric acid (D = 1·838) are cooled with water and ice, 5 c.c. of the oil being then slowly added, with continual cooling. At the end of the reaction the vessel is immersed for 10 minutes in water at 60–65° with constant shaking and then allowed to cool to the ordinary temperature. More concentrated sulphuric acid is next added to drive the unattacked part of the oil into the upper part of the vessel. After centrifugation for 5 minutes and a rest of 12 hours, the volume of the unchanged portion is measured, its refractive index also being determined.

10. Mineral Oils.—Besides by certain alterations of the physical characters, the presence of mineral oils (mostly petroleum of D = 0·75–0·82 and b.pt. 140–190°) in oil of turpentine may be detected as follows.

(*a*) WITH NITRIC ACID. 10 c.c. of the oil are placed in a round-bottomed flask of about half-litre capacity closed with a stopper through which pass a vertical bulb condenser and a tapped funnel. About 30 c.c. of fuming nitric acid (D = 1·52) are gradually added through the funnel, the flask being cooled meanwhile with water and ice and a flow of very cold water maintained through the condenser. The oil of turpentine is converted energetically into soluble products, whereas the mineral oils, at any rate mostly, remain unattacked.

At the end of the reaction, the whole is cooled and the liquid transferred to a flask of about 100 c.c. capacity with a narrow neck graduated in tenths of a c.c. for 10 c.c. The condenser and the original flask are washed out with ordinary concentrated nitric acid (D about 1·4) into the small flask and more of the same acid added until the part of the oil unattacked is

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[1] The correction for each degree is 0·000835.
[2] The correction for each degree is 0·0004.

collected in the graduated part of the neck. After a suitable rest, the volume of this part, which floats on the acid liquid, is measured.

This volume is somewhat less than that of the mineral oil present, since the latter is attacked to some extent by the nitric acid, especially when it contains unsaturated hydrocarbons.

For confirmatory purposes, the unattacked portion is separated and treated again with a few drops of fuming nitric acid—no further reaction should take place. The refractive index (which should be not less than 1·47 at 15° C.) or the refractometric degree (not less than 66 at 15° C.) of this portion is determined.

The acid liquid may be used for the detection of tar oils (*see* paragraph 11).

(*b*) WITH ANILINE. 5 c.c. of the oil and 5 c.c. of recently distilled and very dry aniline are shaken and heated in a test-tube until a homogeneous, clear solution is obtained; a thermometer is then immersed in the liquid and the temperature read when the latter begins to become turbid. With pure oil of turpentine this occurs at 16–25° (at the highest), but, when admixed mineral oil is present, at a higher temperature, usually 26–50°.

If benzene and its homologues are present in addition to the mineral oil, this test is valueless.

11. Light Tar Oils (*benzene and its homologues*).—The presence of these oils, which may have D = 0·870–0·945, b.pt. 80–200° and refractive index above 1·5, exercises a certain influence on the specific gravity, boiling point and refractive index of oil of turpentine. Their presence may also be detected by the test with nitric acid (*see* paragraph 10 *a*).

The action of fuming nitric acid transforms benzene and its homologues (toluene, xylene) into nitro-compounds (nitrobenzene, etc.), which remain in the acid liquid, from which the mineral oil is subsequently separated. The liquid is then diluted with as much water and the solution neutralised with caustic soda solution and extracted with ether. The ethereal liquid (dried with a few granules of calcium chloride and filtered) is evaporated at a gentle heat and the residue weighed. If tar oils are present, this residue will consist of a reddish-brown oily liquid, heavier than water and with the odour characteristic of aromatic nitro-derivatives. The weight found, divided by 1·15 (mean sp. gr. of aromatic nitro-compounds), will give the volume.

12. Light Resin Oils (*Resin spirit or pinolin*).—The presence of these substances, which boil mostly below 170°, increases the amount of the first fraction obtained in the distillation of oil of turpentine; they are also detectable by the following colour reactions:

(*a*) GRIMALDI'S REACTION. 100 c.c. are fractionally distilled slowly and regularly, the first five fractions of 3 c.c. each being collected and then each fraction corresponding with a rise of 5° in the b.pt.—up to 170°. The first five fractions and 3 c.c. of each of the subsequent ones are introduced into test-tubes and treated with 3 c.c. of concentrated hydrochloric acid and a fragment of tin the size of a rice granule, without shaking. The tubes are immersed in a boiling water-bath for 5 minutes and then shaken

vigorously and returned to the bath, being subjected thereafter to occasional shaking.

With oil of turpentine quite free from resin spirit, the liquids remain colourless or assume a tint varying from yellowish to brownish (never green). With oil of turpentine containing resin spirit (even 5%) the acid liquids are coloured orange-yellow and the supernatant oily layers are more or less intense emerald green, according to the quantity and quality of the resin spirit present.

If the coloration is doubtful, 250–400 c.c. of the original product should be distilled, the first 30 c.c. of distillate being redistilled fractionally and each 3 c.c. collected separately.

(b) HALPHEN AND GRIMALDI'S REACTION. As for the preceding reaction, 100 c.c. of the oil are distilled, but in this case the first six fractions of about 1 c.c. each are collected and then fractions corresponding with a rise of 5° in the b.pt. up to 170°. A drop of each fraction is placed in a porcelain dish of about 4 cm. diameter and dissolved in 2 c.c. of a solution of phenol (pure fused phenol, see Vol. I) in carbon tetrachloride (q.v. this volume), the liquid being spread so that the whole of the inner surface of the dish is moistened ; on to the film of liquid thus obtained bromine vapour from a solution of 1 vol. of bromine in 4 vols. of carbon tetrachloride is allowed to impinge. To effect this, a test-tube or conical flask containing the bromine solution is held in a sloping position on the edge of the dish ; more conveniently a special apparatus devised by Grimaldi may be employed.[1] While the bromine is shaken the dish is rotated so that the vapour may come into contact with the whole of it.

With pure oil of turpentine no coloration is observed, even after prolonged action of the bromine vapour ; when admixed resin spirit is present, a yellow coloration appears after a period more or less prolonged according to the amount of resin spirit present. If the supply of bromine vapour is then stopped, the yellow colour gradually changes to green.

In this way as little as 1% of resin spirit may be detected.

13. Pinewood Oil (*Pine spirit*).—This product, obtained either by distilling, in the dry state or in steam or in a vacuum, the wood of various pines, or as a secondary product in the manufacture of cellulose, is a yellowish liquid with a peculiar turpentine-like and sometimes slightly empyreumatic odour, distinct from that of true oil of turpentine ; it has $D = 0.862-0.872$, and it boils gradually from about 155° to 180°, the bulk distilling at 165–175° ; it is dextro-rotatory, a_D being usually 14–22° (10 cm. tube). Its presence in oil of turpentine may be detected by the odour, by fractional distillation (b.pt. gradually increasing with increase of the fractions distilling above 163°) and by the following reactions :

(a) THE SYLVESTRENE REACTION. About 50 c.c. of the oil are distilled, the fraction distilling at about 175° being collected and a few drops of it dissolved in as much acetic anhydride and treated with a drop of pure concentrated sulphuric acid : with pure oil of turpentine, only a yellowish or pink coloration is obtained, whereas, in presence of pinewood oil, which

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[1] *Report of the VIth Congress of Applied Chemistry* (Rome, 1906), Vol. V.

contains sylvestrene (b.pt. about 175°), a violet coloration is formed.

This reaction is shown also by the oil itself, provided it is of recent preparation.

(*b*) HERZFELD'S REACTION WITH SULPHUROUS ACID. From 3 to 5 c.c. of the oil are treated with as much fresh saturated sodium sulphite solution and a few drops of hydrochloric acid (equal volumes of water and the concentrated acid) : if the oil is pure it remains colourless, but if it contains pinewood oil it turns green or yellowish-green. In doubtful cases the test may be repeated on fractions distilling at 155–165° and 165–170°.

Very well refined pinewood oils are not very sensitive to this reaction.

(*c*) THE HALPHEN AND GRIMALDI REACTION. *See* p. 304 : with bromine vapour, pinewood oil gives a carmine coloration, gradually increasing in intensity and tending to violet.

14. Camphor Oil.—Light camphor oil (a by-product in the preparation of safrole), $D = 0.87-0.94$, b.pt. about 170–180°, is especially used to adulterate or replace oil of turpentine. It raises the sp. gr. and the b.pt. of the latter. With the Halphen and Grimaldi, and the Herzfeld colour reactions (*see* preceding section) it behaves much like pinewood oil. It can be identified only when it is contaminated with safrole, which, according to Coen,[1] reacts as follows :

In a distillation flask with a three-bulbed neck, 50–100 c.c. of the oil are distilled, the last 5 c.c. passing over being collected in a flask and treated, drop by drop, with an equal volume of pure concentrated sulphuric acid, the flask being cooled with water and ice to prevent heating. The liquid is then transferred little by little to a tapped funnel containing 20 c.c. of water and cooled with a stream of water, and extracted with 10 c.c. of pure amyl alcohol. The aqueous acid liquid is poured away and the amyl alcoholic layer washed with a little water and then shaken with 5 c.c. of 20% caustic potash solution. In presence of safrole, the alkaline liquid which separates is coloured green or bluish and, when removed, filtered and acidified with sulphuric acid, it becomes violet-red.

Light camphor oils poor in, or free from, safrole do not give this reaction.

15. Carbon Tetrachloride or other Chlorinated Compounds.—These products, having density above 1, increase the specific gravity of oil of turpentine, and lower its boiling point. They may be identified by testing for chlorine as follows :

(*a*) WITH COPPER OXIDE. A piece of copper oxide in the form of wire is fixed to the end of a platinum wire and then heated to redness in a bunsen flame, dipped into the oil and again placed in the flame : in presence of chlorinated compounds, the flame is coloured green.

(*b*) WITH ALCOHOLIC POTASH. The oil is boiled with alcoholic caustic potash solution : this results in the formation and precipitation of potassium chloride, which may easily be identified.

<div align="center">*_**</div>

Genuine oil of turpentine should be colourless, clear, without suspended or deposited extraneous matter, and of normal odour.

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[1] *Ann. Labor. chim. centr. Gabelle,* Vol. VII, p. 99.

Its *specific gravity* at 15° may vary from 0·855 to 0·880, but usually lies between 0·860 and 0·875 ; the specific gravity increases with lapse of time owing to resinification. The presence of mineral oils lowers the density, whilst that of tar oils or chlorinated carbon compounds raises it.

The *boiling point* is 155–175°, but about 80 % should distil below 163° and 90 % below 170° ; old resinified oils boil at higher temperatures. Adulterants alter the boiling point appreciably : resin spirit, light mineral or tar oils, or carbon tetrachloride increase the fractions boiling below 150°, whilst pinewood oils or petroleum increase those between 160° and 170°.

The *refractive index* at 15° is 1·468–1·478 and the reading on the Zeiss butyro-refractometer at 15°, 66–73, most French and American oils having values between 70 and 73 and Greek oil the value 66. Mineral oils lower the refractive index, whilst tar oils raise it.

The *flash point* of the ordinary oil is 32–36°.

The *rotation* varies with the origin : French oils are lævo-rotatory (a_α − 20° to − 40° in a 10 cm. tube), American (+ 9° to + 14°), German and Galician (+ 3° to + 17°) and Greek oils (+ 34° to + 77°) being dextro-rotatory. Venetian or larch oil of turpentine may be either dextro- or lævo-rotatory, while the rotation of regenerated oil of turpentine varies from 0 to about + 7°.

The rotation *is* valueless as regards detection of adulterants, but it may indicate the origin of the oil. It may, however, be noted that mineral oils are virtually inactive and that pinewood oils are dextro-rotatory.

The *residue on evaporation* is scarcely appreciable for the fresh, genuine oil, while crude or old, resinified oil may leave 2 % of residue.

Acidity should be absent from the fresh oil, but old oils are more or less acid.

The *residue on polymerisation* with sulphuric acid should not exceed 1 % (by volume) and the refractive index of this residue at 15° should not be less than 1·5 or the refractometric reading less than 66°.

To the tests numbered 10–15, genuine oils should behave exactly as indicated in the different sections.

An *oil which does not correspond* with any one or more of the physical characters or chemical tests is to be regarded as *adulterated* or *suspect*, whilst one with normal characters may nevertheless be adulterated.

For some purposes (manufacture of varnishes and paints), substitutes for oil of turpentine (pinewood oil, mineral oils) are now admitted, since they are almost or quite colourless and non-fluorescent, while they emit no unpleasant odour, do not alter the tint of varnishes or paints, have the same solvent properties as oil of turpentine and have specific gravities and flash points not greatly inferior.

COLOPHONY

This is the solid residue left when turpentine is distilled for the preparation of oil of turpentine. It consists essentially of resin acids and their oxidation products and forms brittle, translucent masses with a peculiar resinous odour and a colour varying from pale yellow to dark brown ; D = 1·05–1·085. It is readily soluble in alcohol (1 part in 10 parts of 70% alcohol) and dissolves also in methyl or amyl alcohol, ether, acetone, benzene, chloroform, carbon disulphide or oil of turpentine ; in petroleum ether it is not completely soluble. It is easily and completely saponified by caustic soda solution. Addition of a drop of concentrated sulphuric acid to a solution of a small quantity of colophony in acetic anhydride produces an intense violet-red or purple coloration, soon changing to yellowish-brown. Different types or grades of colophony are sold, distinguished mainly by the colour and origin.

Examination of colophony comprises firstly observation of the external characters (colour, transparency, fracture) and comparison of these with those of commercial grades of known origin ; determinations 1–6 may also be carried out to ascertain the degree of purity. Lastly, in order to discover if a product is really colophony and not some similar product such as brewers' pitch, Burgundy pitch, resinates, mixtures of colophony with resinates or with resin oils, fatty oils, etc., tests 7–10 may be carried out.

1. Moisture.—1 to 2 grams of the powdered substance are mixed in a porcelain dish with siliceous sand, previously heated to redness, the whole being then weighed, dried for some hours in a steam-oven and reweighed : loss represents moisture. The drying may also be carried out in a sulphuric acid desiccator, in which the substance is left until of constant weight.

2. Ash.—From 1 to 2 grams of the colophony are carefully charred in a tared dish, which is then heated more strongly either over a bunsen flame or in a muffle to complete incineration. The ash is weighed and then examined to ascertain its nature, tests being made especially for lime, lead oxide, lead chromate, manganese oxide and ferric oxide (*see also* section 9).

Emission of an odour of acrolein during combustion indicates presence of fat.

3. Impurities.—About 5 grams of the powdered colophony are dissolved in 50 c.c. of 90% alcohol and the solution filtered through a filter previously dried at 100° and tared ; any insoluble residue is washed well with cold 90% alcohol, dried at 100° and weighed (*see also* section 10).

4. Melting Point.—This is determined in the usual way in a thin glass tube drawn out at its lower end. When the opaque, white powder becomes brown and transparent, the temperature is read.

5. Acid and Saponification Numbers.—Determined as for fatty substances (*see* Vol. I, p. 374).

6. Paper-sizing Test.—100 grams of the powdered colophony are shaken with 20 parts of crystallised sodium carbonate and 150 parts of water : it is noted whether the mixture is homogeneous and of a milky white or other colour. Finally, alum solution is added and the colour of the precipitate formed observed.

7. Distinction of Colophony from Brewers' Pitch.—*Natural* brewers' pitch—obtained by heating turpentine in open boilers until it ceases to smell of oil of turpentine—may be distinguished from colophony mainly by its appearance, melting point and acid and saponification numbers. Brewers' pitch is usually opaque and brownish-yellow or orange-brown (sometimes, however, translucent or transparent, almost like colophony), and melts at a lower temperature than colophony ; it may indeed easily be made to bind together and is sometimes softened by the heat of the hand. Its melting point, measured as in section 2, usually lies between 40° and 50°. Its acid and saponification numbers are somewhat lower than those of colophony, being usually about 140 and 150 respectively. In all its other characters, however, brewers' pitch is quite similar to colophony.

Brewers' pitch is, however, imitated by colophony coloured with ochre or lead chromate, or by mixtures of colophony with resin oil, fatty oil,

ceresine, or the like. Added mineral pigments are readily detected by their insolubility in alcohol (*see* section 3) or by analysis of the ash; the mixtures mentioned above may be recognised by the tests given in section 10.

8. Distinction of Colophony from Burgundy Pitch.—This resin, obtained by purifying pine or other turpentine by fusing it in water, is distinguished from colophony by the appearance, melting point and content of water.

Burgundy pitch forms almost opaque, hard, brittle masses of lemon-yellow colour and sometimes crystalline appearance. It is softened by the heat of the hand. When dried over sulphuric acid (*see* section 1), it loses a considerable quantity of water—sometimes 35%—whilst colophony contains only traces of moisture.

9. Distinction of Colophony from Resinates.—Resinates of calcium, lead, manganese and zinc, which are the commonest of those obtained by fusion—i.e. by dissolving the corresponding metallic oxide in the colophony fused at a convenient temperature—are very similar in appearance to ordinary colophony, but they are easily distinguishable by determining the ash and by testing their solubility in alcohol.[1]

On calcination, resinates leave an abundant residue (usually 2–20%) of the corresponding metallic oxide. In 95% alcohol they are only partially soluble, but they dissolve moderately well in ether or chloroform.[2]

Similar to the resinates are the so-called *Hardened resins*, consisting of colophony and small amounts of lime or zinc oxide.

10. Recognition of Mixtures of Colophony with Resin Oil, Mineral Oil, Fatty Oil, etc.—Mixtures of colophony (or other resin, especially copal) with resinates, oleates and linseed oil are sold for the preparation of varnishes, and mixtures of colophony with mineral oils, resin oils, fatty oils, solid fats, paraffin wax, ceresine or wax for use as brewers' pitch. For the recognition of such mixtures, the following tests may be made.

(*a*) A little of the substance is heated in a test-tube to ascertain if vapours easily condensable on the cold walls of the tube (mineral or resin oils) are emitted or if an odour of acrolein is evolved (fat). Fat may also be detected by heating with potassium bisulphate and testing with sodium nitroprusside and piperidine (*see* section 6, page 287).

(*b*) A few grams of the substance are incinerated and the ash tested

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[1] Resinates obtained by precipitation, i.e., by treating a solution of alkali resinate with the solution of a metallic salt, are in powder and exhibit no resemblance to colophony.

[2] The quality of a resinate depends especially on the amount of metal combined with the resin, i.e., in the soluble condition. To determine this, a given weight of the resinate is digested in the cold with perfectly anhydrous ether or chloroform, the insoluble part being incinerated and lead, manganese or calcium determined in the ash, according to the kind of resinate. On the other hand, the total ash is determined and the lead, manganese or calcium in it estimated, the soluble metal being estimated by difference. In general the quality of a resinate is enhanced as the proportion of soluble metal present increases. As a rule manganese resinates contain 6–7% of soluble Mn, and manganese oleates 9–9.5% of soluble Mn; mixed lead and manganese resinates contain 8–9% of soluble Pb and 1–2% of soluble Mn. In some cases it is necessary to determine the excess of resin in a resinate, but this can be done only by an indirect method,

especially for lead and manganese, which may be derived from resinates or from linseed oil with a dryer.

(c) The substance is shaken well with approximately 90% alcohol: if solution is not complete, the colophony may contain resinates, fatty oils, wax, solid paraffin or ceresine; by filtration and examination of the part undissolved in the alcohol, the nature of this insoluble matter may be determined. This test may also be made with methyl alcohol, in which colophony containing mineral oils, fats, wax, solid paraffin or ceresine is not completely soluble.

(d) A few grams of the substance are boiled with alcoholic potash and then diluted with water: if a milky liquid is obtained which gradually deposits oily drops, the colophony is mixed with resin oils or mineral oils.

(e) About 10 grams of the substance are dissolved in 100–150 c.c. of ether and the solution well shaken in a separating funnel with about 50 c.c. of dilute sulphuric acid; the aqueous acid liquid is removed and the ethereal solution repeatedly shaken with water until the latter no longer gives a white precipitate with barium chloride solution. The ether is then expelled by evaporation and the acid and saponification numbers of the dry residue determined. If these two numbers are equal, or nearly so, the substance contains no neutral fat, but a saponification number markedly higher than the acid number indicates the presence of neutral fat (mostly linseed oil). In the latter case, one-half the difference between the saponification and acid numbers gives approximately the percentage of neutral fat in the substance.

* * *

Comparison of the *colour and other external properties of colophony* is usually made according to the *American series*, which comprises fourteen different types.

A *good colophony* should yield a white or yellowish powder (not reddish), which keeps dry and soft and does not bind together and agglutinate.

The *moisture* of genuine colophony does not exceed 1%.

Ash exists only in traces, except for small quantities of sand and soil, which are detected by the test of solubility in alcohol (section 3).

Extraneous impurities (sand, soil) should not exceed 1% in the best brands or 2% in the others.

The *melting point* may vary from about 70° to 153°, but is usually 70–80°.

The *acid number* may vary from 145 to 185 (usually 155–170) and the *saponification number* from 155 to 195.

Pure colophony should dissolve completely (except for extraneous impurities) in alcohol or methyl alcohol; it should be entirely saponified by alcoholic potash and the alcoholic solution of the soap should remain clear even when diluted with water.

Colophony for sizing paper should yield (test No. 6) a homogeneous milky-white emulsion, giving a white precipitate on addition of alum.

RESIN OILS

These are obtained by the dry distillation of colophony and are distinguished as *light* and *heavy*.

(A) *Light resin oil, Resin spirit, Pinolin.* Light resin oil consists of the fractions distilling up to about 200°, conveniently refined. It is a colourless liquid of peculiar, more or less empyreumatic and turpentine-

like odour; D = 0·880–0·885; b.pt. = 150–200° (most distils between 150° and 170°). If well refined it is neutral, and it is attacked by concentrated sulphuric or nitric acid; it dissolves in strong alcohol and is recognisable by the colour reactions given on p. 303.

As a rule no special analysis of this product is required.

(B) *Heavy resin oil.* This consists of the fractions passing over above 200°. In the crude state it is dense, turbid, brown, bluish or greenish, more or less fluorescent, acid and with an empyreumatic, resinous odour. The *refined* or *rectified* product is clear, slightly coloured (yellowish or slightly reddish), neutral, or almost so, with a faint resinous odour.

In general, the analysis of heavy resin oils includes the determination of various physical and chemical characters, with a view either to ascertaining its nature and its suitability for definite purposes (*see* sections 1–9), or to estimating its purity or to detecting it in mixtures with other oils (*see* section 10).

1. Physical Characters.—The specific gravity, viscosity, flash point and behaviour at low temperatures are determined by the methods given for heavy mineral oils (Vol. I, pp. 351 *et seq.*). The rotation and the refractive index may also be determined in the ordinary way.

2. Moisture.—Heavy resin oils containing moisture may be turbid or may become so when gently heated; when more strongly heated they give slight explosions.

3. Loss on Evaporation.—20 grams of the oil, in a tared dish, are kept for 5 hours in an oven at 100° and for 2 hours at 170°, the losses in the two cases being determined.

4. Solubility in Various Solvents.—Heavy resin oils are soluble to the extent of 50–100% in double their volume of absolute alcohol; with increase in sp. gr. the solubility in alcohol diminishes. In acetone they dissolve in all proportions (*see also* section 10).

5. Acidity.—This may be due to resin acids, as in crude or incompletely refined oils, or to mineral acids, as in imperfectly washed refined oils.

It is determined as in fatty oils (Vol. I, p. 374) and expressed either as mgrms. of KOH per 1 gram of oil or, more commonly, as SO_3 per 100 grams of oil.

6. Saponification, Resinous Substances.—Resin oils are not saponifiable, except for such part of the resinous substances as they may contain as impurities (especially in the crude oils); these combine with alkali and are detectable by the acid number (*see* preceding paragraph) and by the saponification number, determined as in fatty oils (*see* Vol. I, p. 375).

The content of resinous substances may also be determined directly by saponifying 50–100 grams of the oil with alcoholic potash in the usual way (Vol. I, p. 373), diluting with water, removing the alkaline aqueous liquid, washing the oil remaining unattacked well with hot water and weighing it: by difference the content of resinous substances is determined.

7. Other Chemical Characters.—As subsidiary determinations, the iodine and the Maumené numbers (Vol. I, pp. 379 and 391) may be measured.

8. Colour Reactions.—Heavy resin oils give various colour reactions, due essentially to small quantities of resin present.

(*a*) HOLDE'S REACTION. When equal volumes of the oil and sulphuric acid of $D = 1.60$ are shaken together a red coloration is produced, the acid which separates being coloured red. Mineral, vegetable and terrestrial animal oils give yellowish or brownish colorations, whilst oils of marine animals may give more or less reddish-brown colorations. In doubtful cases the oil in question is shaken with 90% alcohol and the test made on the alcoholic solution : in presence of resin oil the red coloration is obtained also in this way.

Highly refined resin oils give the reaction slightly or not at all.

(*b*) MORAWSKI'S REACTION. 1 c.c. of the oil is dissolved in as much acetic anhydride and the liquid treated with a drop of sulphuric acid of $D = 1.53$: a transitory violet coloration is obtained, provided that the oil has not been perfectly refined.

With mixtures, especially those containing dark mineral oils, it is convenient to heat 2 c.c. of the oil with 10 c.c. of acetic anhydride, the liquid being then diluted with 10 c.c. of water, allowed to cool and filtered through a moist filter : the sulphuric acid is added to the filtrate.

(*c*) HALPHEN'S REACTION. This is carried out according to Grimaldi's directions (this volume, p. 304). Under the action of bromine vapour, resin oil assumes an intense violet or purple coloration. Mineral oils, under the same treatment, given ill-defined brownish colorations, while vegetable and marine animal oils yield red colorations, sometimes tending to violet. It is well to make comparison tests with oils of known origin.

9. Drying Properties.—Heavy resin oils have drying properties : when spread in a thin layer on a strip of glass and kept at 50° for 24 hours, they thicken appreciably and become very tacky.

To enhance the drying properties, various dryers (oxides, resinates or other compounds of lead, manganese or cobalt) are added. In this case, a very dry and hard skin is formed ; the ash may be tested in the usual way for lead, manganese, cobalt, etc.

10. Recognition of Mixtures of Resin Oils with Mineral Oils.—Mineral oil in resin oils may be detected and approximately determined by means of the solubility in a mixture of alcohol and chloroform (Finkener) : A mixture of 10 vols. of alcohol of $D = 0.8182$ (94.5%) and 1 vol. of chloroform is prepared : resin oils dissolve in 10–13 vols. of this mixture at 23° C., whilst mineral oils require more than 100 vols. of the mixture for solution.

To carry out the test, 1 vol. of the oil (10 c.c.) is treated with 10 vols. (100 c.c.) of the above mixture in a graduated cylinder, the whole being brought to 23° C. by immersing the cylinder in a water-bath at this temperature ; the cylinder is then repeatedly shaken and afterwards left at rest. With pure resin oil, solution is complete ; with resin oil mixed with mineral oil, the latter separates at the bottom of the cylinder and its volume, multiplied by 10, gives the approximate percentage by volume.

There are, however, certain resin oils, especially very heavy ones, which do not dissolve completely in 10 vols. of the alcohol-chloroform mixture, 3–7% remaining undissolved. Hence, when a portion does not dissolve under the above conditions, the test should be repeated with 13 vols. of

the mixture : if insoluble oil then separates, the oil really contains mineral oil.

To confirm this, the mineral oil may be washed with approximately 95% alcohol and dried at 100°, its refractive index being then measured at 15° : the value should be below 1·53.

This test may be applied to the detection of mineral oil in complex mixtures of resin oils, mineral oils, fatty substances, soaps, lime, etc., such as cart-grease and stiff lubricants in general (*see* Vol. I, p. 365). In these cases the test is made on the unsaponifiable part after treatment with alcoholic potash to eliminate the fatty and resinous substances, soaps and mineral substances.

On the other hand, for the detection of resin oils in mineral oils or in the unsaponifiable parts of the above mixtures, use may be made of the colour reactions of section 8 and of determinations of certain physical and chemical characters, such as sp. gr., refractive index and rotation—which are higher with resin oils than with mineral oils—and iodine and Maumené numbers, which are almost zero with mineral oils (*see* observations below).

<p style="text-align:center">*_**</p>

Heavy resin oils have the following characters.

Specific gravity 0·97–1·00 ; refined oils, usually 0·97–0·985 (mineral oils not above 0·95).

Viscosity varying from 15 to 100 (with Engler's apparatus at 15° C.).

Flash point about 109–146° with the Pensky apparatus or 148–162° in an open crucible.

Rotatory power + 30° to + 60° in a 10 cm. tube.

Refractive index 1·535–1·555 at 15° C. (mineral oils, 1·48–1·507).

Loss on evaporation in 5 hours at 100° may reach 1·5% (usually 0·4–0·8%) and that in 2 hours at 170°, 5·6–7·4%.

Acidity may be considerable in the crude oils, but should be almost or quite absent from the refined products (*see* below).

The *saponification number* only slightly exceeds the acid number.

The *content of resinous substances* may be 8–10% in crude oils, or 2–4% in those partially rectified ; in well refined oils it should be zero.

The *iodine number* may be about 115 in crude oils, but in the refined product is usually 43–48.

The *Maumené number* of refined oils is usually about 18° to 42°.

As regards resin oils for electric transformers and commutators, the principal requirements are that they should be clear, quite free from moisture and extraneous suspended matters, not acid (up to 0·2% of SO_3 is allowed) and free from mineral oils, and that they should remain quite fluid at −15° C.

Chapter X

VARNISHES

Ordinary varnishes are more or less dense liquids which, when spread on the surface of an object, leave, after a longer or shorter time, a dry, adherent, smooth layer with a continuous, shining surface, which is unaltered by the air or moisture.

They are usually classified as *Volatile* and *Fatty Varnishes*. The former, known also as spirit varnishes, lac varnishes, oil of turpentine varnishes, etc., are solutions of resins and similar products in volatile solvents, while the latter, termed also *oil varnishes*, have as basis drying oils or are solutions of resins or resinates in drying oils, mostly with volatile solvents and often with colouring matters.

In addition to these commoner types, there are many commercial varieties, containing various ingredients, some having for their basis tar, asphalt, rubber, nitro- or acetyl-cellulose, resin soap, borates, dextrin, etc.

The solvents more generally used are : oil of turpentine, pinewood oil, methyl, ethyl or amyl alcohol, amyl acetate, acetone, ether, carbon disulphide, carbon tetrachloride, chloro-derivatives of ethane and ethylene, chlorohydrins, light mineral oils, light oils from tar, from resin or from shale, and camphor oil.

The resins most used are : copal, lac, dammar, sandarac, elemi, mastic, benzoin, amber, colophony and turpentine.

The drying oil most commonly used is linseed oil, but sometimes walnut, poppyseed, sunflower and China wood oils are employed.

The coloured materials most frequently added are : gamboge, dragon's blood, turmeric, indigo, and especially artificial organic colouring matters. For some varnishes mineral colours are used, such as ferric oxide, white lead, minium, lamp black, etc.

The examination of varnish comprises more particularly practical tests and chemical analysis.

1. Practical Tests

These consist in testing the varnish to ascertain its applicability to the purpose for which it is intended. To this end it is spread in a thin layer on a smooth metal (tinned iron) or glass surface and allowed to dry in the air. The time necessary for complete drying and the appearance are noted, and the film of varnish tested to ascertain if it adheres well. After some time the film is observed to see if it has cracked or sweated, i.e., become oily to the touch.

Transparent varnishes are spread over delicately coloured objects to see if the colour remains unchanged.

To test the durability of a varnish, the latter is spread on a sheet of metal; when the film is dry, the metal is heated (e.g., to 100°) and then immersed in cold water. If the varnish does not crack when subjected to this treatment several times, it is of good quality.

2. Chemical Analysis

Complete analysis of a varnish is often extremely difficult. The difficulties are greatest with oil varnishes, these containing drying oils and resins which have been heated so that their physical and chemical characters (solubility in different solvents, density, colour reactions, iodine, acid and saponification numbers, etc.) are changed. Even with simpler varnishes it is difficult to ascertain if they are prepared from a single resin or from several. Minor difficulties are encountered in the determination of the nature of the volatile solvents, although these are sometimes complex mixtures.

In any case, the volatile solvent should first be separated; 50 grams of the varnish, well stirred to render it homogeneous, are mixed with 25-30 c.c. of water in a flask with not too narrow a neck, and the liquid distilled in a current of steam until the volatile substances are separated completely. In general it is sufficient to collect about 100 c.c. of distillate, but the final water condensing should not contain suspended oil drops.

This procedure effects the separation, without decomposition, of the volatile solvent and the fixed residue, which are analysed singly.[1]

1. Volatile Solvent.—Two cases may occur:

(a) *The distillate is clear or only slightly opalescent.* In this case the varnish contains essentially a water-soluble volatile solvent, such as methyl or ethyl alcohol, acetone and some of its homologues. Solvents insoluble or only slightly soluble in water (oil of turpentine, pinewood oil, resin oil, mineral oil, etc.) can be present only in very small quantity. The analysis is carried out as in A (below).

(b) *The distillate is turbid and separates into two layers.* The volatile solvent is evidently insoluble in water. A solvent heavier than water will be carbon disulphide, chloroform, carbon tetrachloride, a chloro-derivative of ethane or ethylene or a chlorohydrin, whilst one lighter than water will be amyl alcohol, amyl acetate, ether, oil of turpentine, pinewood oil, tar oil, light mineral oil, resin oil, shale oil, etc.

It must, however, be noted that when two or more solvents are present, these often dissolve one in the other and do not separate according to their specific gravity.

In any case, in presence of solvents insoluble in water the distillate is

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[1] With some varnishes, especially those with a basis of alcohol, acetone or other solvent soluble in water, it is preferable, in order to avoid useless dilution, to distil directly rather than in steam. 50 grams of the varnish are weighed in a distillation flask provided with a thermometer, and heated on an oil-bath until the solvent is completely eliminated, the temperature being observed meanwhile. The specific gravity of the distillate at 15° is measured and the tests indicated under A applied.

passed into a graduated, cylindrical, separating funnel, the receiver being washed out with a little water into the funnel. After addition of a little powdered sodium chloride and thorough separation into two layers, the volume of the insoluble layer is read and this layer separated from the aqueous one and then washed with a small quantity of water.

The aqueous liquid, which may contain solvents soluble in water, is examined as under *A* and the insoluble layer according to *B*.

(*A*) EXAMINATION OF THE AQUEOUS LIQUID. The aqueous liquid obtained directly in the distillation of the varnish (*see* 1, *a*) or separated from the volatile solvents insoluble in water (*see* 1, *b*) is again fractionally distilled in presence of a little slaked lime, the first 50 c.c. of distillate being collected and its specific gravity at 15° determined. The temperature shown by the thermometer, especially at the beginning of the distillation, may give useful indications concerning the nature of the solvent, which may be identified by the following reactions :

1. *Methyl alcohol.* Methyl alcohol may be detected by the reactions indicated on p. 254. If the aqueous solution contains only methyl alcohol, or this with small quantities of acetone (for detection of acetone, *see* below, paragraph 3), the amount of this alcohol in 100 grams of the varnish may be deduced from the density of the distillate (*see* table, Vol. I, p. 40). If ethyl alcohol (detected as in paragraph 2) also is present, the methyl alcohol is determined either colorimetrically or by combustion (*see* p. 258). The amount thus found is deducted from the total alcohol determined from the density of the distillate by means of the ordinary tables for ethyl alcohol, the remainder being the amount of the latter alcohol.[1]

2. *Ethyl alcohol.* This is detected as follows :

(*a*) A small portion of the aqueous distillate is rendered alkaline with potassium hydroxide and then heated gently with slight excess of a solution of iodine in potassium iodide (1 part iodine, 1 part potassium iodide, 10 parts water). In presence of ethyl alcohol, a pale yellow precipitate of iodoform is obtained, easily recognisable by its smell. Acetone and some of its homologues also give iodoform under these conditions.

(*b*) Another portion of the aqueous distillate is heated gently with a few c.c. of dilute sulphuric acid and potassium dichromate solution. In the vapour emitted is placed a strip of absorbent paper dipped in sodium nitroprusside solution containing two or three drops of piperidine : in presence of acetaldehyde, formed by oxidation of the alcohol, the paper turns blue. Instead of the paper, a pipette with a suspended drop of the nitroprusside solution may be exposed to the vapour, the drop being subsequently absorbed by filter-paper.

If the distillate contains only ethyl alcohol, the amount present is given by the density.

3. *Acetone and its homologues.* Part of the distillate is treated with a few drops of dilute sodium nitroprusside solution and then rendered alkaline

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[1] The densities of methyl and ethyl alcohols and of separate solutions of corresponding concentrations are very nearly equal, so that for approximate determinations the ethyl alcohol table may be used for methyl alcohol or for mixtures of the two.

with potassium hydroxide : presence of acetone is shown by a red coloration, becoming purple on acidification with acetic acid.

For a more rigorous test for acetone and for its determination, the methods given on p. 252 are followed.

The determination of acetone and its homologues in presence of methyl alcohol may be carried out by Messinger's method (Vol. I, p. 40).

(B) EXAMINATION OF THE SOLVENTS INSOLUBLE IN WATER. These may be : carbon disulphide, chloroform, carbon tetrachloride, a chloro-derivative of ethane or ethylene, a chlorohydrin, amyl alcohol, amyl acetate, ether, benzene or a homologue, oil of turpentine, pinewood oil, light mineral oil, resin oil, tar oil, shale oil, or camphor oil.

Many of these solvents, e.g., carbon disulphide, amyl alcohol, amyl acetate, ether, benzene, etc., may be easily identified—especially if unmixed with other solvents—by their odour, density, b.pt. and various reactions (see chapter on Chemical Products, Vol. I, and Tables XXXV and XXXVI, opposite.)

The presence of chloro-derivatives is detectable by the reaction with copper oxide (see p. 305) or by boiling a little of the solvent with alcoholic potash : potassium chloride, readily detected with silver nitrate, is thus formed.

With other solvents, e.g., oil of turpentine, pinewood oil, light mineral oils, resin, tar, shale or camphor oil, the density and boiling point may be determined and various other determinations made, such as the rotation, refractive index, solubility in aniline, behaviour towards fuming nitric acid. The special reactions of resin oil, pinewood oil, shale oil and camphor oil may also be applied.

1. *Specific gravity.* This is measured at 15° with an ordinary hydrometer or picnometer, the solvent being first filtered to remove any traces of water.

2. *Boiling point.* In the ordinary way.

3. *Rotation.* In a Laurent polarimeter (yellow light) in a 10 cm. tube.

4. *Refraction.* This serves especially for the identification of oil of turpentine and for the detection of any added mineral oil ; the determination is made with the Zeiss butyro-refractometer at 15° C. (see p. 36).

For oil of turpentine the value is 66–73 (usually 68–72), whereas light petroleum oils give small values, 0–20 (usually 10–15). Thus a reading lower than 66 is a good indication of the presence of light mineral oil. Refractometric indications are, however, of value only with mixtures of mineral oils and oil of turpentine, the presence of other solvents (e.g., benzene) leading to erroneous results ; thus, benzene gives a refractometric reading of over 100.

5. *Solubility in aniline.* This test also serves for the detection of mineral oil and is made as indicated on p. 303, that is, by mixing 5 c.c. of the solvent with 5 c.c. of pure aniline with a thermometer and heating until a clear, homogeneous solution is obtained. It is then left at rest to cool and the temperature noted at which the solution begins to become cloudy (temperature of turbidity).

6. *Behaviour with fuming nitric acid.* This is the most certain test for

<div align="center">TABLE XXXV</div>

Densities and Boiling Points of Solvents for Varnishes

Solvent.	Sp. gr. at 15° C.	B.pt.	Solvent.	Sp. gr. at 15° C.	B.pt.
Methyl alcohol .	0·790–0·796	64–67°	Carbon tetra-chloride. . .	1·600	76–77°
Ethyl ,, .	0·7942	78–80	Tetrachloroethane	1·600	147
Amyl ,, .	0·814–0·816	129–132	Pentachloroethane	1·700	159
Ether. . . .	0·720–0·722	35–36	Dichloroethylene.	1·25	55
Acetone . . .	0·7966	55–56	Perchloroethylene	1·62	121
Acetone oil . .	0·828–0·842	75–110	Dichlorohydrin .	1·38	174
Amyl acetate .	0·875	138–139	Epichlorhydrin .	1·20	116–118
Carbon disulphide	1·272	46–47			
Chloroform . .	1·49	61–62			

<div align="center">TABLE XXXVI</div>

Characters of Solvents for Varnishes

	Sp. gr. at 15° C.	B.pt.	Rotation in 10 cm. Tube.	Zeiss Butyro-refracto-meter Reading.	Solubility in Aniline.	Behaviour with Fuming Nitric Acid.
Oil of turpentine	0·855–0·880	155–175° (80% should distil below 163°)	From − 40° to + 77°	66–73	Complete (becomes turbid at 14–22°)	Completely attacked
Pinewood oil	0·862–0·872	155–180° (mostly at 165–175°)	From + 14° to + 22°	77–78	Complete	Completely attacked
Light mineral oils	0·750–0·820	120–200°	Inactive	0–20	Incomplete (becomes turbid at 55–70°)	Not attacked
Tar oils . .	0·860–0·900	80–145°	Inactive	More than 100	Complete	Attacked with formation of nitro-derivatives
Resin oil .	0·850–0·950	120–200°	Active	Variable	Complete	Almost completely attacked
Camphor oil.	0·870–0·940	170–180°	Active	61–76	Complete	Completely attacked
Shale oil . .	0·720–0·800	120–200°	Inactive	0–30	Incomplete (becomes turbid at about 50° C.)	Partially attacked

detecting the presence of mineral oils and serves also to detect benzene and its homologues ; it is carried out as indicated on p. 302. If the solvent

contains mineral oils these, remaining unattacked, collect at the surface of the acid liquid and if the whole is transferred into the flask described on p. 302, the quantity may be determined.

If, however, benzene and its homologues are present, these are converted by fuming nitric acid into nitro-derivatives which settle to the bottom after dilution with water. That they are really nitro-derivatives is shown by their odour and by separating them, reducing with zinc and hydrochloric acid and testing for aniline (Vol. I, p. 463).

If the tar oils are accompanied by small quantities of mineral oils, the latter may dissolve in the aromatic nitro-derivatives and so settle to the bottom of the vessel. In such case the deposited layer is separated and distilled in a small flask, only the first portions of the distillate, containing the bulk of the light mineral oils, being collected. This is treated with zinc and hydrochloric acid (cooling somewhat) to reduce the nitro-compounds, and diluted with water : the amines formed dissolve in the water as hydrochlorides and the mineral oils separate as slightly coloured light drops.

7. *Resin oils.* Detected as on p. 303.

8. *Pinewood oil.* This may be recognised by its boiling point (*see* table, p. 317) and by the reactions given on pp. 304–305.

9. *Shale oils.* The identification of shale oils is not always easy. In density, refraction and insolubility in aniline they closely resemble mineral oils, but differ from these in being partially attacked by fuming nitric acid.

10. *Camphor oil.* Identified by the reactions given on p. 305.

2. Examination of the Residue.—From the appearance of the residue obtained on steam distillation, it is easy to decide whether the product is a volatile varnish or an oil varnish. The former leaves a compact, brittle, resinous residue, whereas the latter gives a more or less dense residue with an oily aspect and the odour characteristic of drying oils.

The tests to be made in the two cases are as follows :

(*A*) VOLATILE VARNISH. 1. *Ash.* From 10 to 15 grams of the sample are weighed in a tared porcelain dish, the solvent being then evaporated and the residue charred and subsequently heated for a short time in a muffle at a low red heat. After cooling in a desiccator the ash is weighed, the amount indicating if the varnish contained mineral substances.

The ash is analysed qualitatively : the presence of lead, manganese and calcium indicates the presence in the varnish of resinates, that of sodium carbonate in considerable amount would indicate that the varnish contains soap, whilst boric acid or borates would show the presence of lac rendered soluble by these substances.

2. *Identification of the resins.* This is not very easy as the resins are often mixed and since, in general, resins for varnish making are subjected to special treatment to facilitate their dissolution, the physical and chemical properties being altered thereby.

In cases which are not very complex, some indication as to the nature of the resin may be obtained by evaporating the solvent and testing the residue with the specific reactions of the various resins, observing its behaviour towards solvents and determining its constants, especially the

acid, saponification and iodine numbers. This residue is also tested for the more common substances which may occur in varnishes, such as tar, asphalt, rubber and nitro- and acetyl-cellulose.

3. *Detection of nitrocellulose.* A little of the residue obtained on evaporation of the solvent (*see* above) is treated in a thoroughly dry dish with concentrated sulphuric acid containing in solution a little diphenylamine : in presence of nitrocellulose the intense blue coloration due to nitric acid and nitro-derivatives is observed. Sometimes, however, the nitrocelluloses are partially denitrated, so that the reaction with diphenylamine is feeble ; in such cases test 4, *b* should be carried out.

4. *Detection of acetylcellulose.* (*a*) A little of the residue obtained on evaporation of the solvent is heated gently with concentrated sulphuric acid : in presence of acetylcellulose, the characteristic odour of acetic acid is observed and, on addition of a little alcohol, the pleasant smell of ethyl acetate.

(*b*) A little of the residue is boiled with hydrochloric acid (D = 1·1) and the liquid neutralised and tested for sugar by means of Fehling's solution.

5. *Detection of rubber, tar, asphalt, etc.* The presence of these substances is manifested by the colour (tar, asphalt) and by the characteristic odour emitted when they are burnt.

(*B*) Oil Varnish. The most important tests to be made on these varnishes are those for resinates, resins, mineral colours and thickeners, and those for establishing the characters of the drying oil.

The procedure is as follows :

1. *In absence of mineral matter.* The residue obtained on steam distilling the varnish (*see* p. 314) is collected on a moistened filter and when all the water has run through, the oily residue is poured on to a dry double filter and filtered in an oven at 50–60° into a dry vessel. The filtrate is tested as follows :

(*a*) For dryers. A certain amount of the filtrate is incinerated and the ash tested for lead, manganese and calcium, which are derivable from oleates and resinates.

(*b*) For resin. The oil is shaken with an equal volume of 70–80% alcohol, the liquid being then filtered and evaporated to dryness and the residue tested by the reactions for resin (*see* Vol. I, p. 390).

Oils containing resinates to make them dry well contain a small quantity of resin due to the dryer. Addition of resin may be presumed only when the alcoholic extract is large in amount and the acid number of the filtered oil high (at least exceeding 10–12).

(*c*) Characters of the oil. To establish the characters of the drying oil, the oily residue, freed from resin by treatment with alcohol, is tested as indicated in Vol. I, p. 443.

2. *In presence of mineral substances.* The sample is shaken to render it as homogeneous as possible, about 50 grams being weighed in a conical flask and boiled for some time with 50–60 c.c. of benzene under a reflux condenser. After cooling, the liquid is filtered and the treatment of the residue with benzene repeated two or three times—to exhaustion. The filter retains the mineral colours and other mineral substances added to

give body or special properties to the varnish ; these are analysed separately
in the usual way.   The benzene solution contains the drying oil, resins and
resinates, which are analysed as in the preceding paragraph after evapora-
tion of the solvent.

Chapter XI

RUBBER AND GUTTAPERCHA

Rubber or caoutchouc is obtained by coagulation of the latex of numerous plants belonging to different families, principally to the Euphorbiaceæ, Artocarpeæ and Apocyneæ. Whatever its origin and method of preparation, its value depends essentially on the content in hydrocarbons (*pure rubber*) and on the substances accompanying it (resinous matters, various impurities).

Besides in the *raw* state, rubber is sold also in a purified condition ; these are not generally employed as such, but are first *vulcanised*, i.e., incorporated by suitable processes with sulphur, which imparts special properties.

Rubber articles often contain admixtures of various substances introduced either to give them certain definite characters or as adulterants.

Addition of a large amount of sulphur and of other substances, mostly inorganic, under suitable conditions converts rubber into *ebonite*, which exhibits properties somewhat different from those of ordinary rubber.

Synthetic rubber has been recently prepared, but it has not yet assumed importance as an industrial product. This must not be confused with *rubber substitutes* (principally *factis*), which have been for long in common use, either alone or more frequently mixed with rubber.

Guttapercha, which is similar to rubber, is obtained from the latex of certain of the Sapotaceæ.

The following are some of the principal tests and determinations to be carried out on these products and on objects made from them.

RAW AND PURIFIED RUBBER

Raw rubber is in masses or cakes of form and dimensions varying with the quality and origin, often of stratified section and not rarely containing impurities or occluded extraneous bodies ; it varies in colour from yellowish to brown and has a more or less marked empyreumatic odour ; $D = 0.91$–0.97 ; it is highly elastic, but loses its elasticity when cooled to $0°$ or heated to $60°$; at about $100°$ it begins to soften and it melts at about $180°$ to a blackish liquid, which becomes pasty on cooling but solidifies only after a very long time.

Rubber is insoluble in water, alcohol or acetone ; in ether, benzine, benzene, carbon disulphide, oil of turpentine and certain ethereal oils it swells and gradually dissolves more or less completely.

Purified rubber is in wrinkled or perforated strips, or in blocks, sheet

or leaves; it differs from the raw product in being more compact and homogeneous and in its freedom from occlusions of extraneous matters.

For analysis the sample is taken by cutting strips from various parts of the mass, cutting these again into small pieces and mixing them; the outer part should not be used for analysis, since its composition is often different from that of the interior.

The principal tests and determinations to be made on raw or purified rubber are as follows.

1. Moisture.—The most exact method of determining the moisture consists in drying about 1 gram of the sample, cut into minute fragments and weighed exactly, at the ordinary temperature in a vacuum over sulphuric acid to constant weight, this usually requiring some days; the interval between the two last concordant weighings should be at least 24 hours.

A more rapid but less exact method—owing to the changes suffered by the constituents of rubber on heating and in contact with the air—consists in drying in an oven at 60° C., this usually requiring about 10 hours. Some recommend drying for 4 hours in an oven at 105–110° in a stream of carbon dioxide.

2. Ash.—About 1 gram of the substance (that used for the estimation of the moisture will serve) is carefully incinerated in a platinum crucible, care being taken at the beginning to volatilise most of the organic matter over a small flame.

3. Resinous Substances.—About 5 grams of the substance, exactly weighed, are dried and then extracted in a displacement apparatus with about 150 c.c. of acetone; this extraction is usually complete in 10 hours, but in some cases may require a much longer time. The greater part of the solvent is then distilled from the solution thus obtained, the residue being dried at 80° to constant weight; this gives, with fair approximation, the resin content of the substance.

4. Determination of the Pure Rubber.—Of the many methods proposed, the following may be quoted:

(*a*) SPENCE'S METHOD. The rubber from which the resin has been extracted by means of acetone (*see* section 3) is dried in a vacuum over sulphuric acid to constant weight. An exactly weighed quantity of about 1·5 gram is shaken often and vigorously with about 100 c.c. of cold benzene until dissolved, this usually requiring some hours, but sometimes a few days. The solution is made up with benzene in a graduated flask to 200 c.c., mixed and filtered. For this purpose use is made of a funnel containing a plug of glass wool, the funnel being previously dried at 65° and tared; before the filtration, the glass wool is moistened with benzene and during filtration the funnel is kept covered with a clock-glass.

An aliquot part of the filtrate (100 c.c., or less if the filtration is very slow) is placed in a tared conical flask and most of the benzene distilled off, the rest being evaporated on a water-bath and dried in a vacuum. The residue, representing the *pure soluble rubber*, is weighed and calculated as a percentage on the original substance.

The remainder of the liquid in the 200 c.c. flask is diluted with benzene

(when it is necessary to accelerate the filtration) and the filtration continued through the same funnel. The insoluble matter in the flask is brought on to the funnel, washed with benzene and then with alcohol, dried at 65°, allowed to cool in a vacuum over sulphuric acid and weighed. The proportion of *insoluble rubber* plus any *insoluble impurities* is thus obtained.

(*b*) HARRIES' AND FENDLER'S METHOD. About 1 gram, exactly weighed, of the resin-free rubber (*see* section 3) is dissolved in 75 c.c. of cold benzene in a tared beaker and the solution saturated with nitrous vapours. The latter are obtained by gently heating starch or arsenious anhydride in a flask with nitric acid (D = 1·3). As soon as the development of gas is regular, the flask is closed with a two-holed cork through which pass a tapped funnel and a delivery tube communicating with the lower end of a phosphoric anhydride tower, the upper end of the latter being joined to a fairly wide tube tared with the beaker. The nitrous vapours are passed into the rubber solution for about 2 hours, benzene being added from time to time to replace that evaporated ; in this way the rubber is precipitated as *nitrosite.*

After being left at rest for an hour, the liquid is decanted on to a filter, the beaker and the filter being washed with petroleum ether. The particles of nitrosite from the filter are returned to the beaker and the latter with the tube left in a vacuum desiccator until constant in weight ; the amount of crude nitrosite is thus obtained. The nitrosite is then treated on the water-bath with 50 c.c. of acetone and the liquid filtered through a tared filter, the residue being washed with acetone and dried, and the beaker weighed with the tube and filter : the weight of the residue insoluble in acetone thus obtained is deducted from that of the crude nitrosite, the remainder representing pure nitrosite. 1 gram of *pure rubber* corresponds with 2·125 grams of the nitrosite.

* * *

The composition of *raw rubber* varies according to its botanical and geographical origin and to the method of collection and preparation ; even in the same quality, marked divergences, dependent on various circumstances, may occur.

Raw rubber may contain somewhat varying proportions of *water ;* commercial qualities usually contain about 1–8%, but very poor qualities may have as much as 40%.

Mineral matter—when the rubber does not contain admixtures of sand, clay, etc., owing to careless manufacture or to fraud—is present in small quantity. The best qualities (Parà) leave not more than 0·3–0·6%, but other usual qualities (Cearà, Mangabeira, Negro-head, native African and Asiatic rubbers) from 1 to 4%.

The value of a rubber depends especially on its content of *resinous substances*, increasing as these diminish. Raw rubber contains 1–40%, or even more, of resins. The best American qualities (Parà, good Cearà) contain 1–4% of resin, while the more common American sorts (Mangabeira, Caucho, etc.) usually contain 6–12% or more and the guayule (Mexico), a poor quality, 20–25%. Good African qualities contain 2–12% of resins, but the lower grades may have 20–40% or more. Native Asiatic rubbers of good quality (Borneo, Assam, Manaos, etc.) usually contain 5–20% of resin, but this is greatly exceeded in

the inferior grades. Asiatic plantation rubbers (Parà from Ceylon and Malacca) only contain 1–4% of resin.

The essential and most important component for the properties of the product is the *pure rubber* (soluble), the amount of which varies inversely with the impurities mentioned ; thus, the best American rubbers contain up to 90% (together with a certain quantity of insoluble rubber), other qualities from South America 80–90%, Mexican guayule about 75%, native African and Asiatic varieties 60–85% and sometimes even 90%, and plantation rubbers usually 95% or more.

Purified rubber has been freed from most of the extraneous matter and mineral substances and from almost all the moisture. The washing loss, i.e., the diminution in weight of the raw rubber in consequence of purification, depends on the composition and especially on the content of extraneous matter and moisture : with the best qualities it is scarcely 10% or even less (about 5% for certain plantation rubbers), with good qualities (Parà) 10–20%, and for ordinary qualities 40% or more.

FACTIS

This is the name given to certain rubber substitutes prepared from fatty oils (linseed, cottonseed, colza, cameline, maize, soja bean, arachis, castor, etc., or certain oxidised oils) and sulphur or sulphur chloride. *Brown factis* is prepared by heating the oils with sulphur and usually forms compact, brown, and somewhat elastic masses. *White factis* is obtained by heating the oils with sulphur chloride and forms yellowish-white elastic masses, either light or compact or spongy. Both are insoluble in water or dilute acid and almost so in alcohol or acetone ; they dissolve, but only slowly, in ether, chloroform or carbon disulphide, and are completely saponified by alcoholic potash.

Factis is, however, often sold mixed with various extraneous matters such as mineral substances, mineral oils, vaseline or paraffin wax, resins or resin oils, bitumen, tar, etc. Further, white factis may be coloured artificially by organic colouring matters soluble in fats.

Analysis of these products is carried out as follows :

1. Moisture.— About 5 grams are dried at 100–105° to constant weight.

2. Ash.—About 5 grams are calcined in a porcelain dish.

3. Total Sulphur.—From 2 to 3 grams of the substance are introduced, in small portions, into a porcelain dish containing 20 c.c. of concentrated nitric acid. After about 15 minutes, the dish is placed on a waterbath which is gradually heated, the liquid being evaporated to a syrup and the latter diluted with a few c.c. of fuming nitric acid and again evaporated. The residue is heated carefully to fusion with a lump of caustic potash and a little nitre, the cold mass being dissolved and the sulphuric acid precipitated and weighed as barium sulphate. The percentage of sulphur is thus obtained.

4. Sulphur in the Fatty Acids.—10 grams of the substance are saponified with alcoholic potash and the soap decomposed with an acid, the sulphur in an aliquot part of the fatty acids separating being determined by fusion with caustic potash and nitre and precipitation as barium sulphate. Free sulphur = total sulphur minus sulphur in fatty acids.

5. Chlorine.—From 2 to 3 grams of the substance are heated with concentrated nitric acid and a few crystals of silver nitrate in a sealed tube, the silver chloride thus formed being collected and weighed. The same determination is made on the fatty acids.

6. Substances soluble in Acetone.—From 3 to 5 grams of the substance, weighed exactly and finely divided, are extracted for 4 hours with acetone in a displacement apparatus; most of the solvent is then distilled off and the residue dried and weighed. This residue contains mainly the free sulphur, the fatty oils not combined with the sulphur, and any mineral oils and resin.

The acetone extract may be used directly for the determination of the sulphur (free) and for that of the fatty substances and unsaponifiable substances. Sometimes the sulphur is determined also in the residue insoluble in acetone; this gives the combined sulphur, corresponding approximately with that determined in the fatty acids (*see* section 4).

7. Unsaponifiable Substances.—These are determined as in fats (*see* Vol. I, p. 388).

8. Other Determinations.—These include determinations of the saponification, iodine and acetyl numbers and are made by the ordinary methods (*see* Vol. I: Fatty Substances). As regards the iodine number, as factis is only slowly soluble in chloroform, it must be left in contact with the latter for at least 12 hours with frequent agitation, before the iodine solution is added; further, since factis retains iodine tenaciously, long and vigorous shaking is necessary in the final titration.

<div align="center">**</div>

White factis usually contains 6–9% of *sulphur* and about an equal proportion of *chlorine*, while *brown factis* mostly contains 15–18%, but sometimes much less (3–6%) sulphur. Free sulphur should be small in amount and in general does not exceed 1%.

The *ash*, in good factis not mixed with mineral matter, does not exceed 3%.

The *iodine number* of factis is always much less than that of the oils from which it is obtained; the iodine number of the fatty acids is about three times that of the product itself.

The *saponification number* of factis is usually higher than that of the oils used in its preparation.

As regards addition of other substances, such as mineral oils, to factis, in general these should not be regarded as adulterants, as they may serve useful ends in certain cases when the composition is known exactly; no limit can be placed on the extent of such addition permissible.

VULCANISED AND MANUFACTURED RUBBER

Rubber is vulcanised by treatment with sulphur chloride or by heating with sulphur. In most cases, however, rubber articles are made, not of pure vulcanised rubber, but of the latter mixed with various other substances, organic and inorganic. The organic substances more commonly used are brown and white factis, fatty oils, oxidised oils, waxes, mineral oils, paraffin wax or ceresine, resin or resin oils, bitumens, tar, pitch, starch, and artificial dyes. Very many inorganic compounds may be added either as fillers or to give colour, e.g., talc, kaolin, asbestos, chalk, gypsum, lime,

pumice, glass, silica, clay, graphite, antimony sulphide, cinnabar, minium, litharge, white lead, zinc white, lithopone, barium sulphate, etc.

With these variations and complexities of composition, it is not always easy to analyse manufactured rubber completely or to determine exactly the separate components. The analytical methods to be used vary according to the nature of the product.

The usual tests and determinations are those given below. In every case the sample should be taken so that it represents as far as possible the mean composition of the object ; it should be subdivided into minute fragments.

1. Moisture.—About a gram is dried for 4 hours at 105–110°, preferably in a current of carbon dioxide.

2. Ash.—About a gram is incinerated in a porcelain dish, a small flame being used at first in order to volatilise almost all the organic substances without burning them ; the flame is then gradually raised, care being taken not to heat the residue too much. Even when all precautions are taken, the quantity of ash found represents only approximately the quantity of mineral substances added, owing to the alterations which some of these undergo when heated. The ash is then analysed qualitatively.

3. Total Sulphur.—As in factis (*q.v.*, section 3).

4. Chlorine.—1 gram of the substance is fused with nitre and sodium carbonate, the mass being dissolved in water, the solution acidified with nitric acid, and the chlorine determined either gravimetrically as silver chloride or volumetrically by Volhard's method.

5. Antimony and Mercury.—These, especially the former, may occur in manufactured rubber as sulphides. To determine them, 0·5 gram of the substance and 10 grams of ammonium persulphate are treated in a flask of about 150 c.c. capacity with 10 c.c. of fuming nitric acid. After a few minutes the main reaction is over, the flask being then carefully heated on a sand-bath to complete the attack, 2–3 grams of the persulphate being added if necessary for the oxidation. When nitrous fumes are no longer evolved, the heating is stopped (the whole oxidation does not require more than an hour) and as soon as the mass begins to form crystals, 10 c.c. of hydrochloric acid ($D = 1·124$) are added and then hot water. The liquid is filtered and diluted, and the antimony and mercury precipitated in the ordinary way as sulphides.

In practice sufficiently exact results are obtained by weighing the sulphides freed from excess of sulphur by successive washings with alcohol, ether and carbon disulphide, then dissolving the antimony sulphide in an alkaline polysulphide, and weighing the mercuric sulphide after again removing excess of sulphur.

6. Substances soluble in Acetone.—From 2 to 3 grams of the substance are extracted in a displacement apparatus for 6–10 hours with acetone, the acetone extract being evaporated to dryness in a tared dish and weighed. This residue includes the free sulphur, resins (those of the rubber and those added, except a little insoluble in acetone), fatty oils and waxes, resin oils, mineral oils and paraffin wax.

In the acetone extract the sulphur (free) and the saponifiable and un-

saponifiable substances may be determined and the substances mentioned above tested for by the usual methods.

7. Bitumen, Tar, Pitch.—When these are suspected, the residue insoluble in acetone (without removing the residual acetone) is extracted in the same extractor with pyridine (about 60 c.c.), which is boiled in an oil-bath at about 120°.

The extraction is finished when the thimble holding the substance loses its brown colour and becomes completely decolorised, this requiring 1–2 hours. Excessively long extraction is to be avoided, since an appreciable part of the rubber would then be dissolved. The pyridine solution is evaporated in a tared porcelain dish on an oil-bath, the residue representing the bitumen, tar and pitch of the original substance.

8. Factis and Oxidised Oils.—The substance insoluble in acetone (or if this is treated with pyridine, the residue insoluble in the latter, after washing with acetone) is dried, weighed and boiled for 4 hours with 25 c.c. of N/2-alcoholic potash in a flask under a reflux condenser. If the quantity of factis is very large, the alkaline liquid should be decanted off and the residue treated with a further 25 c.c. of alcoholic potash. The liquid is diluted somewhat with water and filtered through a tared filter, the insoluble residue being washed with boiling water until the wash water passing through is neutral. The filter and residue are dried at 100–105° and weighed : the diminution in weight of the residue represents the factis and any oxidised oils present.

The alkaline solution may be used, if necessary, for various tests and determinations, especially those of sulphur (of the factis) and chlorine (of white factis). From part of the solution the fatty acids may be separated for examination.

Some of the components of commercial factis are soluble in acetone, the amount found as above representing only the quantity of sulphured or chloro-sulphured oils forming the essential components of factis.

9. Pure Rubber and Sulphur and Chlorine combined with it.— In the residue from the preceding determination, that is, in the part insoluble in alcoholic potash, the pure rubber and the sulphur and chlorine combined therewith may be determined by the following methods.

(a) BY EXTRACTION WITH SOLVENTS. The solvents best suited for this purpose are : petroleum (fraction boiling at 230–260°), nitrobenzene (preferably with a little chloroform) and α-nitronaphthalene. With the first two the extraction is carried out at the boiling point, but with α-nitro-naphthalene the substance is digested at 180° with frequent shaking for about an hour. After cooling, excess of ether or petroleum ether (when petroleum or nitrobenzene is used) or benzene (where α-nitronaphthalene is used) is added, the whole being left at rest for 24 hours for the complete deposition of the insoluble substances. It is then filtered through a tared filter or, better, by suction through a Gooch crucible fitted with a double disc of filter-paper, the residue being washed on the filter with the solvent used for dilution, and then dried at 100–105° and weighed. The difference

between the weights before and after treatment with the solvents gives the dissolved substances, i.e., the pure rubber and the sulphur and chlorine combined with it. After elimination of the solvent from the solution obtained, the sulphur and chlorine may be determined.

(b) HARRIES' AND FENDLER'S METHOD. The residue remaining after treatment with alcoholic potash is treated with benzene and left to absorb the latter and swell, the subsequent procedure being as indicated for crude rubber (q.v., section 4, b). In the final treatment with acetone, this dissolves the sulphur and chlorine united with the rubber as well as the pure nitrosite.

10. Mineral and other Inert Substances.—The residue from the preceding determination, i.e., the part insoluble in the solvents of the rubber (or the part insoluble in acetone where the nitrosite method is used), may contain the mineral substances, the carbon and various inert organic substances (starch and other carbohydrates, vegetable textile fibres, etc.). Some of these, such as the fibres, may be recognised by the eye or under the microscope ; the starch may be removed with boiling water and recognised by means of iodine and the mineral matter may be identified by qualitative reactions.

11. Technical Tests.—These are made in addition to the chemical analysis and are briefly as follows :

(a) CHEMICAL TESTS. It is sometimes desirable to test the resistance of the rubber to acids, alkalies, salt solutions, chlorine, oxidising agents, fatty oils or mineral oils. Such tests are made by exposing the sample to the action of these substances, under conditions suitable to each case, at a definite temperature and for a definite time, and noting any changes suffered by the sample.

(b) PHYSICAL TESTS. With some objects permeability to water or gas, or electrical insulating properties are of importance, and with others, the behaviour when heated in the air (at 135° for 2–6 hours) or in superheated steam (at 130–170° for a period of time depending on the circumstances), or exposed to light.

(c) MECHANICAL TESTS. The principal tests are those of the elasticity, resistance to tension, compression, percussion, abrasion and bending ; for each of these tests there are suitable apparatus and standards.

* * *

As regards the chemical *composition* of manufactured rubber, no general data can be given, since the different organic and mineral substances which can be mixed with rubber are allowed or prohibited according to the nature and uses of the object.

In general, a *good rubber* should be homogeneous, compact, flexible and elastic ; it should not exhibit bubbles, and when cut should show a clean, shining surface. It should not alter quickly when stored and to this end it is important that it should not contain more than a minimal quantity of free sulphur ; the addition of factis, especially if this is not well prepared, has an unfavourable effect on the keeping qualities.

EBONITE

Analysis of ebonite is more difficult than that of ordinary vulcanised rubber, as it is less readily attacked by solvents ; the sample for analysis should be finely powdered.   The determinations of moisture, ash, sulphur, etc., are made as in manufactured rubber ; the extraction with acetone should be prolonged, sometimes to 1–2 days, to be complete.   The residue insoluble in acetone is extracted first with epichlorhydrin for 3 hours to remove resins insoluble, or almost so, in acetone (copal, mastic, amber) and then with pyridine as indicated for manufactured rubber ; next comes the treatment with alcoholic potash to dissolve any brown factis present. The residue from this last treatment comprises the pure rubber, the sulphur combined therewith and the mineral matter ; in one part of it the ash and the sulphur of the ash are determined, and in another the total sulphur, the sulphur united with the rubber being obtained by difference ; the pure rubber is then calculated by difference.

GUTTAPERCHA

Guttapercha consists essentially of solid hydrocarbons (*gutta*) and resinous matters (*fluavil, albane*) and may contain also various impurities.   In the raw state it is in masses or loaves of different shapes and sizes ; its colour is from dirty white to reddish brown and it has a peculiar odour ; D = 0·96–1 ; it is not elastic, but is flexible and plastic, its plasticity increasing at about 60–70° C. ; it melts at about 120° and decomposes at a higher temperature. It is an excellent electrical insulator.

It is insoluble in water and partially soluble in anhydrous alcohol or ether ; it dissolves in benzene, carbon disulphide or chloroform and, less easily, in petroleum ether.

The principal tests and determinations made are as follows :

1. Moisture.—As in raw rubber.

2. Ash.—As in raw rubber.

3. Insoluble Impurities.—From 1 to 2 grams of the substance, previously dried, are heated with about 100 c.c. of chloroform in a reflux apparatus on a water-bath, the liquid being afterwards filtered—preferably through a glass-wool filter, previously tared—and the insoluble residue washed with chloroform, dried and weighed.

4. Gutta.—The chloroform solution obtained in the preceding determination is evaporated to about 10–15 c.c. and poured, little by little and with shaking, into a conical flask containing 75 c.c. of boiling acetone, the vessel which contained the solution being rinsed out with a little chloroform and this added to the acetone.   The whole is then boiled for 10 minutes in a reflux apparatus, the gutta, which is precipitated, being thus collected into a mass readily separable from the liquid.   The latter is decanted off and the precipitate collected on a tared filter, washed with acetone, dried and weighed.

5. Resins.—The solvent is distilled from the filtered solution of the preceding determination, the residue—consisting of the resins—being dried and weighed.

6. Technical Tests.—Various technical tests are carried out on gutta percha, the most important bearing on its properties as an electrical insulator.

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The quality of *guttapercha* depends directly on its richness in gutta and on poorness in resins. The most valuable grades, which are rare, contain less than 10% of resins, good qualities 10–20%, and poor qualities more still—sometimes 70%. The good qualities usually contain only small proportions of water (0·5–2%), ash (0·5%) and insoluble impurities (1–5%).

Chapter XII

TANNING PRODUCTS

The tanning materials required to be analysed may be : the prime materials containing the tannin, i.e., bark, wood, roots, leaves, fruit and galls ; liquid or solid extracts obtained from these prime materials ; more or less pure commercial tannins.

PRIME MATERIALS AND TANNING EXTRACTS

Among the *vegetable products* especially rich in tannin and used in tanning are : the bark of the oak (Quercus robur, holm-oak, cork-oak, etc.), chestnut, many acacias (mimosa), birch, many conifers (Norway or common spruce, larch, pine, hemlock spruce), mangrove, eucalyptus (maletto) ; the wood of the oak, chestnut, red quebracho ; the roots of canaigre ; the fruits of algobarilla, myrabolams, babool, divi-divi, valonia ; leaves of sumac ; galls and acorn galls.

Tanning extracts are aqueous decoctions of the preceding and other prime materials, conveniently concentrated and sometimes purified.

Analysis of tanning materials may comprise *qualitative analysis* for detecting and distinguishing them and *quantitative analysis* for the estimation of the proportions of the different components, especially of the tannin.

1. Qualitative Examination

When not powdered, the raw materials may usually be distinguished by their external characters. With powdered materials, the *microscopic* comparison with genuine products often gives useful indications.[1]

The prime materials may likewise be subjected to *chemical examination*, which is the only means applicable to the recognition of tanning extracts ; this is carried out on an aqueous decoction of the raw material or on a conveniently diluted solution of the extract.

The principal reactions and tests used for the identification of different tanning materials and for the detection of adulterations are described briefly below.

1. General Characters and Reactions of Tanning Extracts.— Tanning extracts are liquids, more or less dense according to the concentration, or solids which are brown with either a green or red tinge or more or less pale yellowish brown (purified or decolorised) ; they have an astringent taste and are more or less completely soluble in water. Their dilute

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[1] As regards the microscopic recognition of sumac and its adulterants, *see* U. Brizi, *Staz. sper. agrar. italiane*, 1897, XXX, p. 233 ; Priestman, *Journ. Soc. Chem. Ind.*, 1905, XXIV, p. 231 ; E. Collin, *Journ. de pharm. et chim.*, 1907, XXV, p. 603.

aqueous solutions give with ferric chloride greenish or bluish brown colorations, with zinc chloride dirty yellow precipitates, with ammonium sulphide a pale yellow coloration and a flocculent grey precipitate; they do not form coloured lakes with metallic salts (alum, stannous chloride, etc.), and when subjected to a dyeing test impart to wool only feeble and uncertain tints. These characters, together with determinations of the content of tannin (*see* below, Quantitative Analysis), in general suffice for the recognition of tanning extracts and for their distinction from colouring extracts (*q.v.*, chapter on Colouring Matters). It must, however, be remembered that some colouring extracts (e.g., those of quercitron, catechu and gambier) contain a considerable quantity of tannin and may serve as tanning materials, so that in some cases the distinction between products of the two classes may present difficulty.

2. Distinctive Reactions of Tanning Extracts.—The procedure here given for distinguishing between the principal tanning materials is due to Procter [1] and is based on the treatment of their dilute solutions with certain reagents, which give rise to more or less characteristic precipitates or colorations. Such reactions, however, do not always allow of the certain identification of the different tanning materials, indefinite results being obtained especially with mixtures of different extracts. In any case, to arrive at reliable results it is necessary to work always under similar conditions and if possible to make comparative tests with genuine products.

(*a*) SOLUTION OF THE SUBSTANCE. The reactions are carried out with an aqueous solution of the extract (or an aqueous decoction of the raw material), filtered and diluted so as to contain about 0·6 gram of dry matter per 100 c.c.

(*b*) REAGENTS AND MODE OF USING THEM.

1. *Ferric alum.* A 1% solution is used. To 2–3 c.c. of the tannin solution in a test-tube the reagent is added little by little, excess being avoided; the immediate coloration is noted.

2. *Bromine water.* This should be saturated and is added drop by drop to 2–3 c.c. of the tannin solution until the latter has a distinct odour of bromine: any formation of precipitate, either immediately or after a time, is noted.

3. *Copper sulphate and ammonia.* To 2–3 c.c. of the tannin solution are added a little 1% copper sulphate solution and then excess of ammonia, any precipitate being noted.

4. *Nitrous acid.* To 2–3 c.c. of the tannin solution in a porcelain dish are added excess of freshly prepared sodium or potassium nitrite solution or a few crystals of either salt, and then 3–5 drops of N/10-sulphuric or hydrochloric acid; any coloration is observed and also its subsequent changes.

5. *Stannous chloride.* In a porcelain dish 1 c.c. of the tannin solution is treated with 10 c.c. of a concentrated solution of stannous chloride in

[1] *Journ. Soc. Chem. Ind.,* 1894, XIII, p. 487; see also Allen's *Commercial Organic Analysis,* 4th edit., 1911, Vol. V, p. 44; Procter, *Leather Industries Laboratory Book of Analytical and Experimental Methods,* 1908; Jacomet, *Matières tannantes et cuirs,* Paris, 1911, pp. 9 and 180.

concentrated hydrochloric acid, any colour developed after 10 minutes being noted.

6. *Pinewood and hydrochloric acid.* A shaving of deal is dipped into the tannin solution and then moistened with concentrated hydrochloric acid to see if it becomes red or violet ; such coloration may be manifested either at once or only after some hours.

7. *Sodium sulphite.* A crystal of this salt, placed on a flat porcelain dish, is moistened with a few drops of the tannin solution and any coloration noted.

8. *Sulphuric acid.* About 1 c.c. of concentrated sulphuric acid is carefully added to a few drops of the tannin solution in a test-tube so that the liquids do not mix. The coloration formed at the zone of contact of the two liquids is observed and also that subsequently obtained on mixing and diluting.

9. *Lime water.* Excess of lime water is added to a little of the tannin solution in a flat porcelain dish, any formation of precipitate or coloration being noted, as well as the variations occurring therein after some time.

(c) REACTIONS. The reactions given by solutions of the different tanning materials with the above reagents are shown in detail in Procter's tables, from which Table XXXVII, dealing with the more common tanning materials, is taken. Tanning substances are subdivided into groups, according to their behaviour with certain of the reagents :

Group I includes materials containing tannins derived from pyrocatechol, which give a precipitate with bromine water and a greenish-black coloration with ferric alum. It comprises two sub-groups, with which the precipitate given by copper sulphate (a) redissolves, (b) does not redissolve, in ammonia.

Group II contains tannins of mixed or uncertain nature, the solutions giving a precipitate with bromine water and a bluish-black or purple-black coloration with ferric alum. It is divided into two sub-groups, (a) giving no reaction or, at most, a browning with nitrous acid, (b) giving with nitrous acid a red coloration which tends slowly to purple and afterwards to blue or green.

Group III comprises tanning materials containing tannins derived from pyrogallol, and are not precipitated by bromine water and give a bluish-black coloration with ferric alum. These also are subdivided into (a) those which give the above characteristic reaction with nitrous acid, and (b) those which give no reaction or only a brown colour.

3. Purity of some more Common Extracts.—To distinguish extracts of galls, sumac, oak and chestnut wood, and Norway spruce bark, which are of more particular interest, and to ascertain their purity, the reactions given on p. 334 may be employed, especially those with ferric alum, bromine water, stannous chloride, pinewood and hydrochloric acid, and sulphuric acid ; a dyeing test may also be made. For this purpose a small skein of *white wool* (about 3 grams) is immersed in a dilute solution of the tanning substance (5 grams of liquid extract or 2·5 of dry extract to 250 c.c. of water), the liquid being heated for an hour on a boiling water-bath ; the wool is then wrung out, heated for 15 minutes in 150 c.c. of 1% *potassium*

Characteristic Reactions of the

Substance.	Ferric Alum.	Bromine Water.	Nitrous Acid.	$CuSO_4 + NH_3$.
Group I *a*				
Cutch or catechu .	Green-black	Ppte.	No reaction ; darkens	Ppte. redissolves to red-violet colour
Cork bark. . . .	Green-black coloration	Do.	Reacts somewhat	Ppte. redissolves to brown colour
Green oak. . . .	Do.	Do.	Reacts faintly, if at all	Do.
Garouille (root-bark of Quercus coccifera)	Do.	Do.	Reacts ?	Do.
Quercitron bark . .	Do.	Do.	Reacts somewhat	Do.
Gambier	Deep-green coloration	Do.	No reaction ; darkens	Ppte. redissolves to olive-green
Larch bark . . .	Green-black coloration	Do.	Do.	Do.
Hemlock bark . .	Olive-green reddish ppte.	Do.	No reaction ; pink with $NaNO_2$	Ppte. redissolves to neutral tint
" Larch " extract, from Abies excelsa	Green-black or brown	Do.	No reaction	Ppte. redissolves to olive-green
Group I *b*				
Mangrove bark extract	Green-black	Do.	Do.	Reddish-black
Quebracho wood extract	Green-black coloration	Do.	Do.	Dense ppte.
Chestnut oak . .	Olive-green coloration	Do.	Reacts distinctly	Decided ppte. insol. in excess
Group II *a*				
Stinko or lentisco .	Blue-black ppte.	Do.	No reaction	Dark ppte.
Canaigre	Do.	Do.	Do.	Dense dark ppte.
Mimosa or Wattle barks	Dirty violet ppte.	Do.	Do.	Dense purple-brown ppte.
Group II *b*				
English oak . . .	Blue-black (green with excess)	Do.	Reacts somewhat	Dark brown ppte.
Group III *a*				
Aleppo galls . . .	Blue-black ppte.	No ppte., slight scum	Reacts red to blue	Dark ppte.
Sumac	Do.	No ppte.	Reacts feebly	Dark brown ppte.
Myrabolams . . .	Do.	Do.	Reacts red to blue	Dark ppte.
Pomegranate rind .	Do.	Do.	Do.	Dark brown ppte.
Algorabilla . . .	Do.	Do.	Do.	Dense dark ppte.
Divi-divi	Do.	Do.	Do.	Do.
Valonia	Do.	Do.	Red to blue	Dark reddish ppte.
" Oak wood " extract (oak or chestnut)	Do.	Do.	Do.	Purple-brown ppte.
Group III *b*				
Pure gallotannic acid	Do.	Do.	No reaction	Dark ppte.
Babool pods . . .	Blue-black	Do.	No reaction ; darkens	Dark green colour

XXXVII

more common Tanning Substances

SnCl$_2$ + HCl.	Deal Shaving and HCl.	Na$_2$SO$_3$.	H$_2$SO$_4$.	Lime Water.
No reaction	Deep violet-red	Reddens	Red-brown colour	Reddish ppte. slowly forms
Do.	No reaction	Reddens	Crimson, pink on dilution	Reddish-brown ppte.
Do.	Do.	Do.	Do.	Do.
Do.	Do.	Do.	Do.	Do.
Pale green	No reaction	Doubtful	Do.	Do.
Yellow	Deep violet-red	Yellow	Crimson, brown on dilution	No ppte.
Pink coloration	No reaction	No reaction; darkens	Deep red-brown	Rusty ppte.
Do.	Do.	Reddens	Crimson, pinkish on dilution	Red-brown ppte.
Do.	Do.	Darkens	Deep red-brown	Brown ppte.
Slight reddening	Do.	Slight reddening	Red-brown	Red ppte., darkened by excess
Pink colour, ppte.	Trace	Doubtful	Crimson colour, pink on dilution	Light brown ppte.
No reaction	No reaction	Reddens	Do.	Reddish - brown ppte.
Do.	Do.	Yellow	Yellow-brown	Yellow ppte., darkening
No reaction, clouds	Trace violet	Slight darkening	Do.	Pink coloration, greyish ppte.
Slight reddening	Sometimes trace	Reddens	Crimson, pink on dilution	Reddish or yellow-brown ppte.
No reaction	Faint reaction	Do.	Do.	Reddish - brown ppte.
Light yellow ppte.	No reaction	No reaction	Greenish to dirty yellow	Pale ppte., turning bluish-green
No reaction	Do.	Do.	Yellow	Yellow ppte., turning bright green
Do.	Do.	Yellow	Do.	Yellow ppte., turning greenish
Do.	Do.	No reaction	Orange-brown	Bright yellow ppte., red with excess
Do.	Do.	Deep yellow	Deep yellow-brown	Bright yellow ppte., darkening somewhat
Do.	Do.	No reaction	Crimson	Yellow ppte., turning red-purple
Do.	Do.	Purplish-pink	Deep yellow	Do.
Do.	Do.	Reddens	Yellow-brown	Do.
Do.	Do.	No reaction	Yellow	Pale ppte., turning blue
Do.	Faint violet	Do.	Reddish-violet	Pink colour, no ppte.

dichromate solution at 70° C., washed, and dried. Gall and sumac extrac·
give rather pale greenish-brown tints, those of oak and chestnut purer an
darker browns, and that of Norway spruce a brown but not a reddish-brow
tint.

4. Detection of Adulterations of Sumac.—These consist of th
branches and twigs of the plant itself and also of other plants of less valu
especially Pistacia lentiscus (Stinko or lentisco) and Tamarix african
Among the methods suggested for the detection of such frauds (beside
microscopic examination of the powdered leaves and quantitative deter
minations of the tannins and non-tannins, *see* later), are the following test:
to be made on the solution or aqueous decoction.

The presence of *branches* or *twigs* may be detected by acidifying th
aqueous extract of the suspected sumac with acetic acid : a red coloration
is obtained in presence of these residues, the intensity depending on thei
amount.

The presence of *Stinko* is detected, besides by the precipitate with bromin
water (*see* table), also by the fact that the dilute aqueous infusion (abou
2%) gives with a few drops of formaldehyde in neutral solution a pal
ochre-yellow, flocculent precipitate, subsequently becoming gelatinous
with pure sumac no precipitate forms. Further, when 0·5 gram of th
suspected sumac powder is treated in a dry test-tube with 5 c.c. of caustic
potash solution (20 grams KOH in 100 c.c.) and heated to boiling, th
presence of stinko is shown by a blackish-violet coloration which change:
to brown if the cold liquid is diluted ; in absence of stinko, a brownish-
yellow liquid is obtained, becoming more yellow on dilution.

The presence of *Tamarix africana* is recognised by treating the aqueous
infusion of the suspected sumac with concentrated potassium cyanide solu-
tion : in presence of Tamarix, a dirty yellow, flocculent precipitate is
obtained which is rapidly deposited, whilst with pure sumac no precipitate
and at most a faint turbidity forms.

5. Detection of Sulphur Dioxide.—Sulphurous anhydride, which is
often added to tanning extracts, either as such or more often as sulphites,
to enhance their keeping qualities, may be detected by treating 10 grams
of the extract in a beaker with 20 c.c. of hydrochloric acid and 20 c.c. of
water, a piece of pure zinc being added and the beaker covered with a clock-
glass under which is suspended a strip of lead acetate paper : if the extract
contains sulphurous anhydride, the paper becomes brown or assumes a
blackish tint with metallic reflection. If the paper remains white for 15
minutes, absence of sulphurous acid may be assumed.

6. Extraneous Substances.—Besides being replaced or mixed with
other extracts, tanning extracts may be adulterated with extraneous sub-
stances, such as sugars (glucose, molasses), dextrin, sulphite cellulose liquors
(lignorosin) or mineral salts (e.g., sodium sulphate).

Sugars may be tested for with Fehling's solution in the tannin solution
treated with lead acetate and then with sodium sulphate and subsequently
inverted. Since, however, tanning materials generally contain a certain
quantity of reducing sugars, addition of glucose cannot always be proved
by a mere qualitative test.

Dextrin may be tested for in the liquid treated with lead acetate and sodium sulphate for the detection of sugars : if the latter are absent and the solution is strongly dextro-rotatory, the presence of dextrin is indicated.

The presence of *sulphite cellulosic liquors* may be recognised, according to Procter and Hirst, by treating 5 c.c. of the dilute solution (which is used for analysis) with 0·5 gram of aniline and then, after shaking, with 2 c.c. of concentrated hydrochloric acid : in presence of such liquors a precipitate is immediately formed and gradually rises to the surface.   A more certain indication of the addition of sulphite cellulose liquors may, however, be obtained from a comparison of the results of the determination of the tannin by two methods—indirect and direct (*see* later).

Finally, *mineral salts* may be detected by the ordinary reactions of inorganic analysis.

2. Quantitative Analysis

Quantitative analysis of tanning products (raw materials and extracts) requires firstly rational sampling and then suitable preparation of the sample and solution, and includes mainly determinations of the total soluble matters, the tannins and non-tannins, water and insoluble substances.[1] Other determinations sometimes made are those of the ash, sugar and sulphurous anhydride, and in industrial practice the specific gravity and colour of the solutions are often measured.

The principal methods for the quantitative analysis of tanning materials are given below.

1. Sampling.—The samples for analysis should be taken from at least 5% of the casks, bags, baskets, lumps, etc., comprising the bulk, the following points being observed :

(*a*) EXTRACTS.   With liquid extracts, the contents of each cask are first well mixed so as to detach from the bottom and walls any adherent deposit, while solid extracts should be broken up so that samples representing the whole mass may be taken.   With gambier and other extracts in lumps, the sample is taken from each piece by means of a tubular instrument, with which the mass is perforated at different points so as to pass completely through it ; a similar procedure is followed with pasty extracts.   In any case the separate portions should be rapidly mixed and placed in a tightly closed vessel to prevent action of the air and evaporation.

(*b*) PRIME MATERIALS (bark, wood, etc.).   The contents of the different bales chosen for sampling are spread out on a flat surface in so many superposed layers, samples being taken at different points of the mass and perpendicular to the surface from top to bottom ; if such procedure is not possible, samples are taken from the central part of each heap and thoroughly mixed.   In some cases these samples are ground before sending

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[1] For these determinations and for the preliminary operations mentioned, the directions laid down by the International Association of Leather Trades Chemists are officially adopted in Europe.   These specify also that the results should always represent the mean of two distinct and concordant analyses.   The official methods used in America are those of the Association of Official Agricultural Chemists of the United States and of the American Leather Chemists' Association and differ in some details from the European methods (*see* Allen's *Commercial Organic Analysis*, 1911, 4th edit., Vol. V, pp. 76 *et seq.*).

them to the chemist, but this is not advisable with certain products, such as divi-divi and algarobilla.   If one and the same sample is to be examined by different chemists, a large sample is taken, well mixed, and divided into portions.

2. Preparation of the Sample for Analysis.

(*a*) LIQUID EXTRACTS.   Immediately before weighing, liquid extracts should be thoroughly mixed in all directions.   Very dense extracts, which cannot be well mixed, are heated to 50° and stirred, a portion being then removed for analysis, cooled rapidly and weighed ; if such an operation is found necessary, this is indicated in the report of the analysis.   In any case the weighings should be made rapidly to avoid loss of moisture.

(*b*) SOLID AND PASTY EXTRACTS.   Solid extracts are coarsely powdered and then well mixed.   Pasty extracts are mixed rapidly in a mortar and the portion for analysis weighed as rapidly as possible to prevent loss of moisture.

If the extracts are partly dry and partly moist, the whole sample is weighed, allowed to dry completely at the ordinary temperature, powdered and again weighed, the loss of weight (moisture) being allowed for in the calculations.

Where, as with gambier, it is not possible, either by grinding or by other mechanical means, thoroughly to mix the whole sample, it is allowable to dissolve all the sample or a large part of it in a small amount of water, to remix well and to weigh for analysis part of the concentrated solution.

(*c*) BARK AND OTHER SOLID TANNING MATERIALS.   The whole sample, or a quantity not less than 250 grams, is ground so that it passes completely through a sieve of four meshes per cm., i.e., 16 per sq. cm.   If, as with certain barks and with divi-divi, fibrous parts are present which cannot be so finely ground, the ground sample is sieved and the sieved portion and that remaining on the sieve are weighed separately and proportional quantities of the two taken for analysis.

3. Preparation of the Solution.—The concentration of the solution of the substance should be such that it contains as nearly as possible 4 grams of tanning material per litre and in any case between 3·5 and 4·5 grams.[1]

[1] To obtain the prescribed concentration, a preliminary test must be made if there is no indication of the approximate content of tannin in the substance.   In general this concentration is obtained approximately by weighing out, for each litre of solution, the following quantities of the different tanning materials (*see Journ. Soc. Chem. Industry*, 1904, XXIII, p. 458):

	Grams.		Grams.
Solid extracts	5–7	Pine bark	32
Pasty extracts (D above 1·2)	9–12	Garouille	16
Fluid extracts (D above 1·15)	12–18	Hemlock bark	32
Do. do. (D below 1·15)	18–20	Chestnut wood	45
Algarobilla	9	Galls and acorn galls	12
Canaigre	18	Mimosa bark	12
Divi-divi	9	Mangrove bark	10
Oak bark	36	Myrabolams	12
Oak wood	50	Quebracho wood	22
Sumac	16	Willow bark	36
Valonia	14	Used materials	50
Trillo	10		

In the case of tanning materials or liquids already used, a solution containing if

(*a*) LIQUID EXTRACTS. The necessary quantity of the extract, weighed in a covered dish or open beaker is well shaken with boiling water in a litre measuring flask and is then made almost up to the mark with boiling water (with extracts of sumac and myrabolams it is better to use water at a rather lower temperature). The liquid is cooled rapidly to 17·5° C., made up to the mark, shaken and filtered (*see* below, section 4).

(*b*) SOLID EXTRACTS. Solid extracts are dissolved in a beaker by shaking with boiling water, the liquid being transferred to a litre flask and the undissolved parts repeatedly treated with fresh quantities of boiling water. When all the soluble matter is dissolved, the procedure is as with liquid extracts.

(*c*) SOLID RAW MATERIALS. The amount of material necessary to obtain a solution of the concentration indicated is extracted first with 500 c.c. of water at a temperature not exceeding 50° (preferably after maceration for some time with cold water) ; the extraction is then continued with boiling water to a volume of 1 litre.[1] The whole extraction should last at least 3 hours ; the small quantities of soluble substances which may remain in the materials are neglected or in some special cases they are subsequently extracted and estimated separately as *substances difficultly soluble*.

4. Total Soluble Substances.—After *filtration*, a measured volume of the solution prepared as described above is *evaporated*.

(*a*) *Filtration.* The tanning solutions should always be filtered, even when they appear clear. This is carried out at a temperature of 15–20° either by means of a Berkefeld candle, or a paper 17 cm. in diameter, or otherwise. Whereas the candle and also some qualities of paper do not absorb substances from the solution provided that the first 250–300 c.c. of filtrate are discarded, other qualities of paper and other filtering media may absorb them in appreciable quantity, a correction being necessary in this case (*see* below). If necessary, the later portion of the filtrate (after rejection of the first portion) is returned several times to the filter until it is clear—a luminous object, such as the filament of an incandescent electric lamp should be distinctly visible when viewed through a thickness of 5 cm. of the liquid, and a layer of the liquid 1 cm. deep, placed in a beaker on a sheet of shining black paper and viewed from above in good light, should appear dark but not opalescent.

The mean correction necessary for the absorption by the filter is determined by filtering, according to the above directions, two portions of the same tanning solution, one through a filter which does not absorb and the other through the filter in question. The difference between the total soluble substances in the two cases—determined by evaporation—gives the necessary correction. The mean of at least five such determinations is to be taken as the mean correction to be applied for the given filter.

possible 3·5–4·5 grams of tanning substances per litre is obtained by diluting the solution or by concentrating it in a vacuum or in a vessel with limited access to the air ; in no case should the solution contain more than 10 grams of total soluble substances per litre.

[1] Such extraction may be conveniently carried out in a displacement apparatus, such as that of Procter (*see Journ. Soc. Chem. Ind.*, 1892, XI, p. 331) or Koch (*see Leather*).

(*b*) *Evaporation.* In a flat-bottomed dish, prevously tared, 50 or 100 c.c. of the perfectly clear filtrate are evaporated on a boiling water-bath. The residue is dried to constant weight in a steam-oven (at 98·5–100°) and left to cool in a desiccator over calcium chloride before weighing. The result obtained is calculated for 100 parts of the material.

5. Non-tanning Matters.—For this determination, the tanning substances are absorbed from the solution by hide powder, the liquid being then filtered and the dry residue estimated in the filtrate. The *detanning* of the solution may be effected by one of the two following methods.

(*a*) By Shaking. 1. *Preparation of the chromed hide powder.* The hide powder to be used should be of woolly and non-granular appearance and should be freed from lime by means of hydrochloric acid ; 6·5 grams of the dry powder, suspended in water, should not require more than 5 c.c. or less than 2·5 c.c. of N/10-alkali to give a permanent pink coloration with phenolphthalein. If the acidity of the hide powder does not lie between these limits, it should be corrected by adding the necessary quantity of standard alkali or acid to the water with which the powder is moistened prior to the chroming (*see* below), the powder being left in contact with the liquid for 20 minutes. Further, the hide powder should not swell on imbibition so as to render it difficult to reduce its water-content to 70–75% by pressing. It should also be so free from soluble matter that, when washed with distilled water, 100 c.c. of the wash-water does not leave more than 5 mgrms. of dry residue on evaporation.

The moisture in the hide powder, dried in the air and stored in a tightly closed vessel, is then determined (good commercial powder should not contain more than 14%) and the quantity of the air-dry powder equivalent to 6·5 grams of the dry powder calculated. A multiple of this weight is taken, in accordance with the number of analyses to be made, and moistened with about 10 times its weight of water (or a little more if the powder is very woolly). A basic chromium chloride solution is also prepared by dissolving in water 2 grams of crystallised chromium chloride ($CrCl_3$, $6H_2O$) for each 100 grams of the dry hide powder and adding 0·6 gram of anhydrous sodium carbonate or 11·25 c.c. of N-sodium carbonate solution. If many analyses are to be made, 100 grams of the chromium chloride are dissolved in a little water, a solution of 30 grams of anhydrous sodium chloride being then added gradually and with stirring and the volume made up to a litre ; 20 c.c. of this solution are required per 100 grams of the dry hide powder or 1·3 c.c. per 6·5 grams of powder. The powder, moistened as stated above, is treated with the necessary quantity of chromium solution and left for an hour. It is then well squeezed through a cloth and washed repeatedly with distilled water, pressing each time, until addition of a drop of 10% potassium chromate solution and 4 drops of N/10-silver nitrate solution to 50 c.c. of the filtrate yields a brick-red coloration (usually after four or five washings) : when this is the case, the 50 c.c. of filtrate contain not more than 0·001 gram of sodium chloride. Finally the washed chromed hide powder is pressed until its water content is 70–75% and the whole weighed.

2. *Determination and filtration.* A quantity *q* of the moist chromed

hide powder, corresponding with 6·5 grams of dry hide powder, is weighed and introduced at once into 100 c.c. of the unfiltered tanning solution, to which is also added (26·5–q) c.c. of distilled water ; in this way, taking the water in the hide powder as water of dilution, the 100 c.c. of solution may be regarded as made up to 120 c.c. The vessel is well closed and shaken for 15 minutes either by hand or mechanically, but in either case with at least 60 rotations or shakes per minute. The mass is then squeezed at once through cloth and the liquid shaken with a gram of kaolin free from soluble matter (this may be added beforehand to the hide powder) and filtered through a pleated filter, large enough to contain the whole of the solution, until a perfectly clear filtrate is obtained ; part of this should not be rendered turbid by a drop of a solution containing 1% of gelatine and 10% of sodium chloride.

3. *Evaporation.* 60 c.c. of the filtrate (corresponding with 50 c.c. of the tanning solution) are evaporated on a water-bath and the residue dried in a steam-oven and weighed : this represents the non-tannins and is calculated as a percentage on the original substance.

(*b*) FILTER METHOD. In this method, due to Procter, the special apparatus shown in Fig. 64 is employed. It consists of a glass bell *c* of the dimensions indicated in Fig. 65,[1] to which is joined, by means of a rubber stopper, a siphon tube *d* of bore not exceeding 2 mm. ; the end of the siphon projecting into the bell is closed with a little cotton-wool or glass-wool. In the bell are placed about 6–7 grams of the hide powder,[2] which is distributed so that it is neither too loose nor too tight ; it should be rather tighter at the walls than in the middle of the mass (a little practice is necessary to ensure this).

FIG. 64

The mouth of the bell is then covered with a piece of well washed gauze or muslin, which is kept in place by a rubber ring.

The bell is then placed in a beaker *a* of about 200 c.c. capacity so that the covered mouth of the bell almost touches the bottom of the beaker. Into the latter a little of the tanning solution is poured and when this has all been sucked up by the hide powder (usually in about an hour), the beaker is filled with the tanning solution and the siphon filled with the liquid by suction at its free end. The liquid flows slowly from the siphon so that the efflux of about 100 c.c. requires 1·5–2 hours.

The effluent is first caught in a beaker—until a drop of it fails to turn turbid with a clear tannin solution ; as a rule at least 30 c.c. must be collected.

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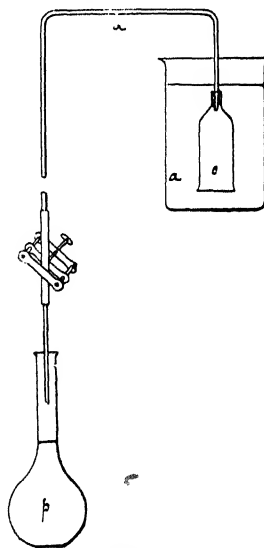
[1] The bell may be replaced by a glass cylinder or a bottle without a bottom.
[2] Various qualities of hide powder have been recommended for this determination ; in general, a powder answering the requirements already indicated for the preceding method may be employed. Also in this case some prefer to use a chromed hide powder, which will give more concordant results.

About 60 c.c. are then collected separately in a flask ; this should be colour-less, or almost so, and a few drops of it, treated with a solution of gelatine and sodium chloride (or with some of the initial distillate, which contains a small quantity of gelatinous substances and is a good reagent for the detection of tannin), gives no turbidity.
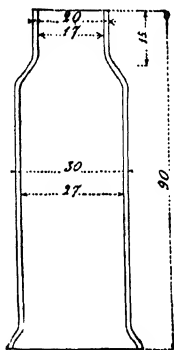
Of this second portion 50 c.c. are evaporated in a tared dish on a water-bath, the residue being dried in a steam-oven to constant weight. It represents the non-tanning substances and is calculated per 100 grams of the original substance.

This method was used officially by the International Association of Leather Trades' Chemists before the shaking method was introduced (1907), and is still often used in practice, especially by manufacturers of extracts.

Fig. 65

6. Tanning Substances.—These may be found by difference or determined directly by various methods.

(*a*) INDIRECT METHOD. The tanning substances are calculated as the difference between the total soluble matter and the non-tannins (*see* above, sections 4 and 5).

This method is prescribed by the International Association of Leather Trades' Chemists.

(*b*) DIRECT METHODS. Of the many methods which have been proposed for this purpose but are now rarely used, only Schröder's modification of Löwenthal's method—one of the best known—will be described. It is based on the reducing power of tannin towards permanganate, indigo being used as indicator as it is decolorised only after all the tannin has reacted with the permanganate. Since tanning products generally contain non-tanning substances capable of reducing permanganate, the quantities of the latter consumed by the solution before and after detanning with hide powder must be determined : the difference between the two quantities is that consumed by the tannins.

Necessary reagents. (1) Solution containing 10 grams of potassium permanganate in 6 litres.

(2) Indigo solution prepared by dissolving 30 grams of solid indigo carmine (sodium indigosulphonate) in 3 litres of dilute sulphuric acid (1 : 5 by volume), adding 3 litres of water, shaking and filtering. For each titration 20 c.c. of this solution are diluted with about three-quarters of a litre of water ; normally this should reduce about 10·7 c.c. of the permanganate solution, the actual amount being determined by **preliminary titration**. For this purpose 20 c.c. of the indigo solution are diluted as stated above and the permanganate run in from a burette, at first 1 c.c. at a time and with vigorous shaking for 5–10 seconds after each addition ; when the liquid becomes pale green only 2–3 drops of permanganate are added at a time, these additions being carried out carefully—with shaking as before —until the liquid assumes a distinct golden-yellow coloration.

It is most important to operate always under the same conditions, both when determining the titre of the permanganate and when actually estimating the tannin.

(3) Hide powder : this should be white, woolly and free from any substances soluble in cold water and capable of reducing permanganate—this is shown by a blank test.

(4) Tannin, as pure as possible (*see* later) and dry ; in case of doubt, the moisture may be determined by drying at 100°. A solution containing 2 grams of dry tannin per litre is prepared.

Titre of the permanganate.   20 c.c. of the indigo solution are added to 10 c.c. of the tannin solution (containing 0·02 gram of tannin) and the liquid diluted and titrated with the permanganate in the way described above. Subtraction from the number of c.c. used of that required by the indigo solution gives the quantity of permanganate consumed by the tannin solution.

It is, however, necessary to investigate the quality of the tannin used. For this purpose, 50 c.c. of the same tannin solution are placed together with 3 grams of hide powder in a flask with a ground stopper, the flask being frequently shaken over a period of 18–20 hours ; the liquid is then filtered and 10 c.c. of the filtrate titrated as above. If the quantity of permanganate used in this second titration (less that corresponding with the indigo) does not exceed 5% of that consumed in the first titration, the tannin is suitable.

Calculation is then made of the titre of the permanganate, i.e., the weight of tannin corresponding with 1 c.c. of the permanganate solution, by dividing the quantity of tannin (0·02 gram) by the number of c.c. consumed by the tannin in the first titration, this value being corrected on the basis of the second titration. Thus, if the result of the latter is about 5% of that of the first, the above titre is multiplied by $\dfrac{100}{95}$ or, with sufficient accuracy, by 1·05.

Determination of the tannin.   The solution of the substance for this determination may be made like those already indicated (*see* above, section 3), but should be more dilute, so that 10 c.c. of it reduce 4–10 c.c. of permanganate : about 5 grams of a solid extract, 10 grams of a liquid extract or of a rich material like sumac, or 20 grams of an ordinary bark are taken per litre of solution. The liquid is filtered if necessary.

To 10 c.c. of the tanning solution prepared in the above conditions are added 20 c.c. of the indigo solution, the mixture being then diluted with three-quarters of a litre of water and titrated with permanganate, as already described, to a distinct golden-yellow colour. To another quantity of 50 c.c. of the same solution are added 3 grams of hide powder ; after about 18 hours, during which time it is occasionally shaken, the liquid is filtered and 10 c.c. of the filtrate titrated in the same conditions as before.

The difference between the volumes used in the two titrations gives the amount of permanganate corresponding with the tannin absorbed by the hide from the 10 c.c. of solution taken. The titre of the permanganate being known, the percentage of tannin in the substance is readily calculated.

Löwenthal's method gives results which are not very concordant in all cases and are not comparable with those of the indirect method.

With tanning extracts adulterated with cellulosic extracts, the indirect method does not, however, give reliable results, since cellulosic extracts contain non-tannins which are fixed by the hide powder. In such a case the tannin should be determined by the direct method, since these non-tannins have no appreciable action on permanganate ; the difference between the results of the two methods will give an approximate indication of the extent of the adulteration, if this is at all marked.

7. Total Dry Extract, Moisture and Insoluble Matter.—In a tared flat dish are weighed exactly 1–2 grams of the substance, which are dried in a steam-oven (98·5–100°) to constant weight ; after cooling in a desiccator over calcium chloride the dry residue is weighed.

With extracts a measured volume (50 or 100 c.c.) of the turbid, homogeneous (unfiltered) solution prepared as indicated in section 3 may be evaporated in the tared dish on a water-bath and the residue dried as before.

In every case the *dry residue* found is calculated as a percentage of the substance, the deficit from 100 being *moisture*.

Finally the *insoluble matter* is calculated by subtracting the total soluble matter from the total dry residue.

8. Ash.—About 5 grams of the substance are carefully charred in a platinum dish over a small flame, the residue being incinerated at a dull red heat. Sometimes it is necessary to lixiviate with hot water the carbon obtained, to incinerate the residue, add the aqueous solution, evaporate and calcine.

If the ash is large in amount, it may be examined qualitatively to detect any addition of mineral salt.

9. Sugars.—A solution of such concentration that it contains not more than 1% of sugars (with extracts, 6–16 grams are usually dissolved in 200 c.c.) is used ; 200 c.c. of this solution are shaken with 20 c.c. of basic lead acetate, left for a quarter of an hour, and filtered through a dry filter. Of the filtrate, which should not give any further precipitate on addition of basic lead acetate, 100 c.c. are treated with 10 c.c. of sodium sulphate solution of concentration corresponding with that of the lead acetate, shaken, left to settle and filtered. The reducing sugars (regarded as glucose) are determined either gravimetrically in 25 c.c. of the filtrate by means of Fehling's solution or volumetrically, the methods described in the chapter on Sugars (*q.v.*, General Methods) being used.

If saccharose (molasses) is present, another portion of the defecated and filtered solution is inverted by the usual procedure and the determination of the reducing sugars repeated. From the difference between the results before and after inversion, expressed as invert sugar, the saccharose is calculated by multiplication by 0·95.

10. Sulphurous Anhydride.—The total sulphurous anhydride (free and combined) is determined by distilling a few grams of the extract (weighed exactly), after dilution with water and treatment with a little phosphoric acid. The distillate is caught in a solution of iodine in potassium iodide, in which the sulphuric acid is subsequently precipitated by barium chloride

in presence of hydrochloric acid ; from the barium sulphate obtained the sulphurous anhydride is calculated.[1]

11. Specific Gravity.—The sp. gr. of tanning solutions is determined (usually at 15° C.) with the Westphal balance or with a hydrometer or, in industrial practice, with the Baumé hydrometer.[2]

12. Colour.—This is measured, when necessary, with the *Lovibond tintometer*,[3] in which the colour of a layer of solution of definite thickness is compared with that of a series of coloured glasses of definite tints and intensities, these being combined so that they give the same tone and the same intensity of colour as the solution. The colour is then expressed in arbitrary degrees of red, yellow and black.

⁎
⁎ ⁎

The value of tanning products depends primarily on their content of tanning substances (tannin), but their mode of employment depends also on the quantity and quality of the non-tannins they contain.

The *tannin content* of different raw materials varies considerably, according to the quality and origin, as is seen from the examples quoted in the following table (XXXVIII), which gives also the soluble non-tannins and the reducing sugars.

With Sicilian *sumac*, comparison of the composition with those of its principal adulterants (Stinko and Tamarix) shows that a sumac containing less than 22% (or at the least 20%) of tannin and more than 18% (or at most 20%) of soluble non-tannins is to be regarded as adulterated.

As regards *extracts*, their composition varies greatly according both to the methods of preparation and purification and to the degree of concentration. With these the possibility of adulteration, especially with glucose, molasses, cellulose extracts and mineral salts, is to be considered. Addition of sulphurous anhydride or sulphites is allowed, for either clarification or preservation of the extract ; the proportion of total sulphurous acid may reach and even exceed 2%.

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[1] For further particulars, *see* Wine (p. 211) and Beer (p. 169).

[2] For definite qualities of raw materials the specific gravities or degrees Baumé of the solutions are sometimes used in industrial practice to deduce, from suitable tables compiled empirically, the approximate content in tannin and in total soluble matter.

[3] *See* Procter, *Leather Industries Laboratory Book of Analytical and Experimental Methods*, 1908.

TABLE XXXVIII

Compositions of Certain Tanning Materials

Material.	Tannin, %.		Non-tannins, %.		Reducing Sugars, %.	
	Mean.	Limits.	Mean.	Limits.	Mean.	Limits.
English oak bark . . .	10·1	6–16	6·6	5–13	2·7	1·8–3·5
Green oak bark	—	5–11	—	—	—	—
Cork oak bark	11·0	10–15	—	—	—	—
Garouille	26·0	24–28	8	—	1·0	0·7–1·5
Spruce bark	11·6	7–16	10	6–15	3·5	2·7–4·5
Larch bark	—	6–13	—	—	—	—
Hemlock bark . . .	12·3	8–16	—	—	0·7	—
Mimosa bark	32·0	21–50	7	2–12	0·9	0·3–1·6
Mangrove bark	35·0	—	6	3–14	—	—
Eucalyptus (maletto) bark .	40·0	35–52	7	—	—	—
Oak wood.	—	5–12	—	—	0·5	0·4–0·6
Chestnut wood	—	5–10	—	—	0·3	0·2–0·4
Quebracho wood	22·0	15–26	1·6	—	0·4	0·1–0·7
Canaigre	30·0	25–35	15	9–18	6·8	—
Algarobilla	43·0	35–52	20	—	8·2	6·2–10·5
Myrabolams	30·0	16–46	14	10–18	5·4	3·2–7·1
Divi-divi	41·5	25–51	18	15–20	8·4	7·9–8·8
Valonia	29·0	14–38	12	9–14	2·7	1·2–3·6
Do. (Trilla) . . .	44·0	35–55	14	—	2·4	—
Sicilian sumac . . .	26·0	22–31	16	15–18	4·5	4·4–4·6
Stinko or Lentisco . . .	15·0	12–17	—	20–27	—	—
Tamarix africana . . .	10·0	8–15	—	23–26	—	—
Levant galls	60·0	50–70	—	—	—	—
Bassora galls (red) . . .	29·0	23–36	7	5–9	1·1	0·7–1·5
Istria galls	40·0	—	—	—	—	—
Italian galls	—	10–20	—	—	—	—
Chinese and Japanese galls .	—	50–77	—	—	—	--
Acorn galls	30·0	21–38	6	5–7	0·6	0·5–0·7

TANNIN

Commercial tannins are more or less pure according to the method of preparation, the purest being those termed *ether* and *alcohol tannins*, those known as *water tannins* being less pure. The most common impurities of these tannins consist of insoluble matter, inorganic substances, resinous substances, reducing sugars, chlorophyll and gallic acid ; extraneous matters which are added are dextrin, starch and magnesium sulphate.

The analysis of tannin, as far as the determination of the soluble, insoluble and tanning substances are concerned, is carried out, when required, by the methods already described for tanning products in general. It includes also the following tests and determinations.

1. Solubility.—1 gram of the tannin is dissolved in 5 c.c. of water and

the solution observed to ascertain if it is clear and the depth of its colour. 5 c.c. of 90% alcohol are then added to see if the solution remains clear and, if this is so, 2·5 c.c. of ether are added to ascertain if any turbidity is thus occasioned.

On the other hand, 1 gram of the tannin is dissolved in 5 c.c. of alcohol to see if the solution obtained is clear and if it remains so on addition of an equal volume of ether.

2. Moisture.—5 grams of the tannin are dried in an oven at 100° to constant weight.

3. Ash.—The dry residue from the determination of the water is carefully incinerated and the ash weighed and then tested to ascertain if it is soluble in 90% alcohol.

If the ash is large in amount, it is analysed qualitatively, especially for sulphuric acid and magnesia, marked quantities of these showing adulteration with magnesium sulphate.

4. Reducing Sugars.—The tannin is dissolved in water, the solution clarified with lead acetate and filtered, the filtrate being tested with Fehling's solution for reducing sugars, which may also be determined quantitatively.

5. Chlorophyll.—The tannin is shaken with equal volumes of water and ether : if chlorophyll is present, the ether assumes a greenish coloration.

6. Gallic Acid.—The aqueous solution of the tannin is treated with potassium cyanide solution : in presence of gallic acid, a red coloration (or a transitory pink coloration, if the gallic acid is very small in amount) is formed, this disappearing on standing and returning on shaking.

7. Dextrin and Starch.—The tannin is well shaken with 80% alcohol, the liquid being filtered and the residue washed with alcohol of the same strength and then taken up in water. In the case of dextrin, this dissolves in the water and the solution is coloured red by tincture of iodine and has a marked dextro-rotation. If the residue is starch, this does not dissolve in the water, turns blue with iodine, and may be identified microscopically.

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The *purer tannins*, such as alcohol and ether tannins, are completely soluble in alcohol and in water, giving slightly coloured solutions ; the aqueous solution is not rendered turbid by addition of alcohol and then of ether, or the alcoholic solution by addition of ether (*see* above, paragraph 1). They leave little ash (less than 0·5%), which is soluble in 90% alcohol. They contain 95–100% of tannic acid.

The water tannins give with water more or less coloured solutions, and with alcohol more or less turbid solutions ; they leave an appreciable amount of ash (1·5% or more), which is almost insoluble in 90% alcohol. Their content of tannic acid rarely exceeds 92% and is sometimes much less.

Finally, tannins should not be adulterated with sugars, dextrin, starches or mineral salts.

CHAPTER XIII

INKS

Black writing inks may be classified according to their composition as follows :

(*a*) *Inks with a basis of tannic and gallic acids and iron.* These inks (from galls and the like) are the oldest and contain compounds of iron (rarely of vanadium) with tannic and gallic acids ; these compounds give the black colour and are held in suspension in the liquid by means of thickening agents, such as gum, dextrin and sugars.

(*b*) *Alizarin, anthracene inks, etc.*, which do not, however, contain these tar derivatives, but are also based on iron tannates or gallates, these being held in solution by means of acids, especially in the case of gallates. These inks are more fluid than the preceding and give writing which is only faintly coloured when fresh, but becomes darker on exposure to the air ; this inconvenience is usually avoided by the presence of a colouring matter, such as indigo carmine or other organic colour.

(*c*) *Inks based on logwood and a chromium* (alum, chloride, oxalate), iron or copper salt. They do not usually contain thickening agents and give writing which is reddish or violet at first and becomes blacker on drying and exposure to the air.

(*d*) *Aniline inks*, which are aqueous solutions of certain coal-tar colours (nigrosin, indulin, diamine black, etc.) with addition of a thickener.

Mixed gall and logwood inks and inks based on lamp-black, humous matters, etc., are also common. Copying inks contain also glycerine, glucose, calcium chloride, in order that the writing may not dry too quickly. Some inks, termed carbon inks, contain either gum lac or colophony held in solution by means of borax or sodium carbonate, or casein or sodium silicate (in such inks the colour is mostly obtained from lamp-black).

Indications of the nature of an ink are obtained by qualitative tests (*see* section 1, below). To determine its value for the required purpose, the more important components of the ink are determined quantitatively (*see* section 2) and various practical tests are made (*see* section 3).

1. Qualitative Tests

1. Extract and Ash.—A certain quantity of the ink is evaporated in a porcelain dish on a water-bath, the appearance and colour of the extract being noted ; part is kept for further investigations and part calcined to determine the ash.

During the calcination the odour of the vapours evolved is noted— that of burnt sugar, resin, acrolein, artificial organic dyes or vegetable

extracts, according as the ink contains sugars, resins, fatty substances, coal-tar colours or logwood.

The ash obtained is then analysed qualitatively by the ordinary methods, especially for iron, copper, chromium, aluminium, calcium, magnesium, vanadium and alkali. Iron occurs in abundance in the ash of gall inks; copper is found, usually in small quantities, in iron gallate or tannate or logwood inks; chromium may be present in the ash of logwood inks as oxide or as alkali chromate (in the latter case the ash is yellowish and gives a yellow solution with a little water). Aluminium, calcium and magnesium may be derived from the materials used for the preparation of the ink; calcium may also be due to the presence of calcium chloride (in copying inks), while magnesium comes more especially from the gum (gum arabic or senegal). Alkalis, especially potash, are found in the ash of inks prepared with chrome alum. Vanadium is tested for particularly when the ash is small in quantity and does not contain iron, while other tests indicate a gall ink; the ash is fused with potassium nitrate and the mass taken up in water and treated with hydrogen peroxide, which gives a red coloration in presence of vanadium.

2. Chlorides, Sulphates, Oxalates.—A small quantity of the ink is diluted with water so as to give a slightly coloured, clear liquid.

One part is acidified with dilute nitric acid and tested for chlorides with silver nitrate.

Another is acidified with dilute hydrochloric acid and treated with barium chloride for the detection of sulphate. Barium chloride is added until no further precipitate forms and the liquid filtered, the filtrate being neutralised with soda or potash and again filtered; the filtrate is treated with acetic acid and calcium chloride: if a white precipitate forms, this is separated and identified as calcium oxalate.

Chlorides or sulphates occur in gall or logwood inks prepared with iron or chromium chlorides or sulphates and in copying inks containing calcium chloride. Oxalates occur especially in logwood inks prepared with chromium oxalate.

3. Acetic Acid, Acetates and Ammonia.—An ink containing free acetic acid smells of it, especially when boiled in a test-tube.

To detect acetates, occurring especially in logwood inks based on chromium acetate, a portion of the ink is acidified with dilute sulphuric acid and distilled in a current of steam, the distillate being tested for acetic acid.

To test for ammonia—sometimes added to neutralise excessive acidity—a portion of the ink is rendered alkaline with potash and boiled to ascertain if ammonia is evolved.

4. Behaviour towards Sulphuric Acid.—This test, which gives an indication of the nature of the colouring matter of the ink, is carried out as follows: A small quantity of the ink is diluted with water to give a non-opaque solution, dilute sulphuric acid being then added and the changes in tint observed.

The liquid becomes decolorised or assumes a yellowish tint, sometimes slow to appear: ink composed only of galls and iron.

The liquid, at first bluish, becomes distinctly azure : presence of indigo.

The liquid assumes a red tint : probable presence of logwood.

The liquid does not change or becomes green or another colour, or gives a precipitate : probably ink with artificial organic dye or of varied nature.

5. Detection of Logwood.—The presence of logwood is presumed from the red coloration obtained with an acid (*see* preceding paragraph). As a confirmatory test, a portion of the extract (*see* section 1) is heated with alcohol slightly acidified with dilute hydrochloric acid and filtered ; the filtrate is tested by means of the following characteristic reactions of logwood.

Potash in excess is added : the red solution becomes deep blue and after some hours brownish.

Part of the liquid is neutralised exactly with potash, the alcohol being expelled and the residue taken up in water. With alum the aqueous solution slowly turns bluish-red and then violet ; with copper sulphate and sodium acetate it gives an intense blue coloration, and with lead acetate a blue precipitate.

6. Tannic and Gallic Acids.—A preliminary test for these two acids may be made by diluting the ink with water, acidifying slightly with dilute sulphuric acid and extracting with ethyl acetate. The ethereal liquid is evaporated and the residue dissolved in water, the solution being tested as follows :

With freshly prepared gelatine solution tannic acid, but not gallic acid, gives a precipitate ; with potassium cyanide solution, tannic acid remains unaltered whereas gallic acid gives a red coloration.

When it is necessary to test for both acids—this is rarely required, especially with tannin inks, which always contain gallic acid—the following procedure may be employed :

From 2 to 3 c.c. of the ink are diluted with 5–6 vols. of water and treated with excess of 20% sodium acetate solution, which precipitates the iron tannate but leaves the gallate in solution. After some time the liquid is filtered and the precipitate washed on the filter with the same sodium acetate solution until the liquid passes through the filter colourless.

The precipitate (tannate of iron) is dissolved in dilute sulphuric acid and the solution thus obtained extracted with ethyl acetate, the ethereal liquid being then separated from the aqueous solution and evaporated to dryness. The residue (tannic acid) is dissolved in water and identified by means of dilute ferric sulphate or ferric alum solution (blackish-blue coloration). If the ink contains logwood, part of this passes with the tannin : in such case, to identify the tannin in the aqueous solution of the ethyl acetate extract, distinctly alkaline ammoniacal copper sulphate is added, this giving a precipitate in presence of tannin.

The solution in sodium acetate, containing the gallate of iron, is acidified with dilute sulphuric acid and extracted with ether, the ethereal liquid being separated and evaporated to dryness and the residue (gallic acid) dissolved in water. If this solution really contains gallic acid, it should give : an intense blue coloration with ferric sulphate ; a red coloration—disappearing on standing and reappearing on shaking—with potassium

cyanide; a white precipitate with tartar emetic; no precipitate with gelatine. If the ink contains logwood, part of this passes with the gallic acid; the latter is then identified by treating the aqueous solution of the ethereal extract with sodium aluminate (obtained by dissolving a large excess of aluminium hydroxide in caustic soda) and so expelling the logwood.

7. Detection of Indigo Carmine and Artificial Organic Dyestuffs. —A small quantity of the ink is diluted with water and divided into two portions, one being acidified with a few drops of hydrochloric acid and the other rendered alkaline with a little ammonia; in each a strand of wool is suspended and the liquid heated, not too strongly, for about 15 minutes. The wool is then removed and well washed with hot water.

If the wool is intensely coloured, the presence of artificial organic dye or of indigo carmine is probable. In this case the operation is repeated in an acid or alkaline bath according to which gives the more intensely coloured wool; the colouring matter is then extracted from the wool and identified by the methods described for artificial organic dyes (*see* Chapter XV).

Indigo carmine is fixed by wool in an acid bath and may then be removed from the wool by boiling this with dilute sodium carbonate solution. The solution thus obtained gives the following reactions: with sulphuric acid, a blue coloration; with potash it decolorises somewhat; with stannous chloride it becomes decolorised in the hot (the colour reappears on addition of ferric chloride); by nitric acid or chlorine water it is decolorised (the colour cannot be restored in any way).

8. Dextrin and Sugars. The ink is diluted somewhat with water and treated with basic lead acetate to eliminate any gum present. After filtration, the excess of lead is eliminated by means of hydrogen sulphide and a large amount of alcohol then added; any dextrin is precipitated in whitish flocks, which are allowed to settle and then dissolved in water. This solution should give a marked dextro-rotation and should become reddish when treated with tincture of iodine.

Sugars are tested for in the dextrin-free solution by means of Fehling's solution, before and after inversion with hydrochloric acid.

9. Gum.—The ink is strongly acidified with hydrochloric acid and diluted with 2-3 vols. of alcohol. After 1-2 hours the precipitate is collected, this consisting of gum if dextrin and sugars are absent. The gum is characterised by the rotation and by the pentosan reaction: The precipitate is dissolved in hydrochloric acid ($D = 1.19$) and the solution divided into two parts; one is boiled with a little phloroglucinol, which gives a reddish-violet coloration in presence of gum; the other is heated somewhat and when cold treated with a few drops of pure aniline, which gives a crimson coloration (furfural) in presence of gum.

10. Glycerine.—The ink is evaporated to a syrup, which is taken up in 96% alcohol and the liquid filtered; the alcoholic solution is evaporated and the residue tested for glycerine as follows: A few drops are heated in a test-tube with a crystal of potassium bisulphate. In presence of glycerine, the irritating odour of acrolein is observed and a spot of sodium nitro-

prusside and piperidine solution on a rod is coloured an intense blue (care must be taken to eliminate the whole of the alcohol).

11. Various Antiseptics.—Arsenic or mercury compounds, carbolic acid, salicylic acid or thymol are sometimes added to inks to prevent fermentation and mould growth.

Arsenical or mercury compounds are detected by evaporating a quarter of a litre of the ink and heating the extract with 1–2 c.c. of concentrated sulphuric acid and 5–10 c.c. of fuming nitric acid until nitrous vapours are eliminated, the addition of nitric acid and the heating being repeated until a perfectly colourless liquid is obtained (Rothe). The sulphuric acid is then expelled and the residue tested for arsenic and mercury by the ordinary analytical methods.

Organic antiseptics (carbolic and salicylic acids) are recognised by evaporating the ink, mixing the residue with sand and extracting with ether. The ethereal solution is evaporated and part of the residue tested for carbolic acid—already detectable by its odour—by precipitating with bromine water as tribromophenol. The other part is dissolved in water, the solution shaken with a mixture of 1 part of ether and 1 part of petroleum ether, and the ethereal liquid evaporated to a volume of a few c.c. ; the hot residue is mixed with a few drops of very dilute ferric chloride solution and the whole poured on to a moist filter. The aqueous solution passing through the filter is violet if salicylic acid is present.

2. Quantitative Analysis

Quantitative analysis is carried out almost exclusively on tannin and gallic acid inks, since only for these have limits been established for certain of the components. It comprises principally the following determinations.

1. Extract.—10 c.c. of the ink are evaporated to dryness in a platinum dish on a water-bath, the residue being kept for an hour in an oven at 100° and weighed.

This determination and the following may serve for the identification of an ink when a sample is available for comparison.

2. Ash.—The extract obtained above is burnt and the residue calcined, a few crystals of ammonium nitrate being added if the carbon is difficult to burn.

3. Acidity.—With gall inks or mixed inks containing iron salts, it is necessary to eliminate the iron before determining the acidity. For this purpose, 5–10 c.c. of the ink are placed in a 100 or 200 c.c. flask, diluted somewhat with water and treated with potassium ferrocyanide solution (quite neutral) until no further precipitate is formed. The whole is then made up to volume with water, shaken and allowed to settle, an aliquot part of the clear liquid being pipetted off and the acidity determined by titration with N-KOH solution (indicator, phenolphthalein).

With a logwood and chromium ink, without tannin or iron, the acidity may be determined directly (after convenient dilution) without addition of indicator, by adding standard potash solution until the violet colour

changes to blue (a few preliminary trials admit of the exact determination of the point at which the tint changes).

The acidity of an ink is expressed in c.c. of N-KOH per 100 c.c.

The acidity may be regarded as a criterion of the corrosive action of the ink on pens, although this is influenced by the nature of the acid—organic or inorganic, fixed or volatile, etc.

Better evidence on this point is obtained by a practical test, a pen being dipped in the ink three times a day for a definite number of days (e.g., 10) and allowed to dry spontaneously each time, the final condition of the pen being examined.

4. Iron.—This is determined by one of the following methods :

(*a*) 10 or 20 c.c. of the ink are evaporated and the residue incinerated. The ash is dissolved in hydrochloric acid and the iron precipitated with ammonia and filtered off, the precipitate being washed, ignited and weighed. If aluminium is present the iron in the precipitate is determined volumetrically.

(*b*) 10 c.c. of the ink are heated with ammonia and 20 grams of ammonium persulphate on a water-bath, 5 grams of sodium acetate being added and the liquid boiled. The separated ferric hydroxide is filtered off, washed, and either ignited and weighed or dissolved in hydrochloric acid and titrated with permanganate.

5. Tannic and Gallic Acids.—These two acids are determined together by the following method (Rothe and Hinrichsen) [1] : 10 c.c. of the ink are shaken in a separating funnel with 10 c.c. of concentrated hydrochloric acid, the liquid being then extracted four times with 50 c.c. of ethyl acetate.[2] The separated ethereal liquids are shaken in another separating funnel two or three times with a half-saturated solution of potassium chloride (10 c.c. each time) to remove any iron salts present. The ethereal solution is evaporated in a vacuum and the residue taken up in a little water, evaporated in a tared dish, dried in an oven at 105° and weighed. This gives the total tannic and gallic acids (anhydrous) in 10 c.c. of the ink.

To ascertain if the residue really consists of these two acids, an aliquot part of it (about 0·1 gram) is treated with 2 grams of sodium bicarbonate and 25–50 c.c. of a solution of iodine in potassium iodide (containing about 50 grams of iodine per litre and of known titre with respect to thiosulphate), the whole being then left for 12 hours in a bottle with a ground stopper. The excess of iodine is then titrated with the thiosulphate in presence of starch paste and that absorbed by the acids calculated ; 0·1 gram of gallic and tannic acid of galls absorbs 0·6–0·7 gram of iodine.

3. Practical Tests

1. Keeping Qualities.—A certain quantity of the ink is placed in a glass beaker (18–20 cm. high and about 7 cm. in diameter) covered with a filter-paper and observed after some time (a month or more) to ascertain

[1] Hinrichsen : *Mitt. aus dem Kgl. Materialprufungsamt*, 1906, 24.

[2] Where many successive determinations are to be made, the extraction may be facilitated by using Rothe's apparatus, which is described in the above paper and consists of a double separating funnel.

if mould has developed.   About 25 c.c. of the filtered ink are left in another beaker for a certain number of days ; it is then examined to see if any deposit has formed or if any forms when the residue is made up in the beaker to its original volume.

The bottles containing the ink are also examined for mould and deposit.

2. Writing Tests.—These are made with a good new pen, well defatted, thick and thin lines being traced on a good, perfectly absorbent, but not too highly sized, paper.   Note is made if the ink flows well from the pen or if it is too dense or if it falls in drops.   Further, the lines should be uniform and should not spread or pass through the paper ; no border of various colours should appear after some time.   The time necessary for complete drying is noted and observation made of the colour—whether black at first or becoming so only after exposure for some time to the air.   When the ink is quite dry, its resistance to washing with water and with 85% alcohol is tested.

A writing test is also made by stretching a good sheet of paper in a kind of frame which keeps it taut.   The sheet is placed at an angle of $45°$ to the horizontal and a given quantity of the ink allowed to flow on to it from a pipette with a very narrow orifice so as to form a streak ; three days later the streak is examined to see if it is dry, what the colour is and how it resists the action of air, light and different reagents.

The above tests, especially the last and particularly when a gall ink is being examined, are advantageously made in comparison with a *standard ink*, such as is used in some States for documents.

Such an ink may be prepared by dissolving 23·4 grams of pure tannin and 7·7 grams of gallic acid in about 500 c.c. of tepid water and then adding 30 grams of ferrous sulphate, 10 grams of gum arabic and 2·5 grams of hydrochloric acid,[1] each dissolved in water.   The whole is made up to 1000 c.c. with water, well shaken, and left to settle for four days in a cool place ($10-15°$) ; if the materials used were pure, no sensible deposit is formed.

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Of all *inks*, the best and the most resistant to the action of light and atmospheric agents are those made from tannic and gallic acids, logwood and iron inks showing less resistance and aniline inks none.

Inks to be used for records to be kept for long periods should be made solely from tannic and gallic acids with addition of a suitable quantity of thickening ; they should be fluid and not turbid and should contain between 4 and 6 grams of iron and 25 grams of gallic and tannic acids together per litre ; for these inks the use is allowed of indigo carmine or other colouring matter to enhance the tone of the writing immediately it is written.   They should not give a deposit within 15 days or mould within 40 days ; they should give distinct writing which not later than 3 days afterwards should be perfectly black and dry and should resist without appreciable change washing with alcohol and with water. Their acidity should be normal and such that pens are not affected in 10 days when tested as described above.

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[1] Such a quantity of dilute hydrochloric acid, of known concentration, as corresponds with 2·5 grams of HCl, should be weighed or measured.

CHAPTER XIV

LEATHER

Leather represents the product obtained by subjecting the hides of animals to suitable processes (tanning) to give them keeping properties and to impart to them certain special qualities (elasticity, flexibility, etc.).

According to the animal furnishing the hides and to the consistency and uses, leathers are distinguished as *heavy leathers* or leather proper (sole, belting leather) and soft leathers (for vamps, saddlery, trunks, etc.). Further, according to the system of tanning used, *tanned, chromed, tawed* (with alum) or *oil*-tanned leather is obtained. Finally, according to the treatment employed after tanning, the leather may be fat-liquored, dyed or enamelled.

The complete and systematic examination of leather, including physical and mechanical tests [1] and chemical analysis, is carried out principally for tannin- or chrome-tanned leathers. The methods to be used in this examination are given below and are preceded by the procedure to be followed in sampling.

Sampling.—With whole hides, a certain number are taken (at least 5%, from which, if very numerous, a smaller number are chosen) and from each of them pieces are removed from different parts (rump, hind quarter, shoulder, flanks, belly) in proportions corresponding as far as possible with the extent of each part. If this cannot be done, the sample is taken from the shoulder, which in composition and characters resembles the whole hide more closely than any other part.

When the sample is to be taken from manufactured articles (e.g., shoes), portions are removed in suitable amounts from each of a number of the articles.

Part of the sample (about 100 grams), to be used for chemical analysis (*see* later), is then reduced to small pieces and these by means of a suitable mill to a woolly powder ; when this is not possible, as with oiled leather, the sample is cut with a knife into very small fragments. The sample thus prepared is kept in well closed vessels.

TANNED LEATHER

1. Physical and Mechanical Tests

These include, besides examination of the external characters, determinations of the specific gravity, strength and permeability, and sometimes microscopical investigation.

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[1] For these *see* Boulanger : *Essais du cuir* (Mémoires publiés par la Soc. d'encouragement p. l'ind. nation., Paris, 1907).

1. External Characters.—The appearance of the surface of the leather is examined on both faces—the smoothness, grain, colour, presence of spots, cuts, holes or other defects. The leather is bent on itself to ascertain if it cracks and breaks or remains unaltered.

The appearance of the section is then examined to see if it is compact and homogeneous or spongy and if the colour is dark and uniform ; light lines parallel to the surface are often an indication of an unequal distribution or an incomplete penetration of the tanning material.

The section is best examined by cutting strips 2 or 3 cm. long, 2 mm. wide and 0·5 mm. thick between two cuts normal to the thickness of the hide, these strips being immersed for 15 minutes in 20% acetic acid and their appearance then observed. In well tanned leathers the sections do not appear transparent and are swollen little and uniformly, whilst those of badly tanned leather swell considerably in the parts which have not absorbed the tanning material completely, so that the surface no longer appears uniform ; when viewed by transmitted light they exhibit a pale, shining striation in the middle.[1]

2. Specific Gravity.—This may be determined by cutting a square of the leather of about 10 cm. side, measuring the dimensions exactly and the thickness in different parts by means of micrometer calipers, and calculating the volume from the area and the mean thickness : sp. gr. = (weight in grams) ÷ (vol. in c.c.).

Another method consists in cutting a strip of leather 25–30 cm. long and 1–2 cm. wide, weighing it and immersing it in a graduated cylinder containing mercury, in which in some way it is kept submerged ; the increase in volume is then read.

The moisture content of leather exerts a marked influence on the specific gravity, concordant results being obtained only by referring the weight of the piece used for this determination to a normal moisture-content (18%) and then calculating the specific gravity. The latter may also vary largely with the proportion of fatty substances present.

Lastly, since the specific gravity varies with the region of the hide from which the sample is taken, the determination should be made on pieces taken from different parts and the mean result adopted.

3. Strength.—*Tension* tests are the most usual, these being made by means of a dynamometer like that used for textiles, strips of the leather of definite length and breadth (usually 1–2 cm. wide according to the quality and thickness) being tested. The resistance to breaking, expressed in kilos per sq. mm. of section, and the percentage elongation are measured.

In some cases *compression* tests are also made.

Of importance also is the *flexibility* test, which is carried out by bending a strip of the leather (bloom outside) into an arc, at first with a diameter equal to ten times the thickness and afterwards with less diameters (the strip may be bent round cylindrical rollers of different diameters), any cracking and the depths of the cracks being observed.

4. Permeability.—The object of this test is to determine the greater

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[1] To cut sections of the thickness indicated and to observe them more easily, suitable forms of apparatus have been constructed.

or less facility with which the leather is penetrated by water. Of the various methods of carrying out the test, the following may be quoted.

(1) The weight of water absorbed by imbibition by a given weight of the leather is determined. For this purpose a piece of the leather, previously weighed (about 20 grams) is placed in a flat dish and covered completely with water. At successive intervals of an hour it is withdrawn, carefully dried outside, weighed and re-immersed, this procedure being continued until no further increase in weight occurs. The weight of water absorbed is referred to leather with a normal moisture content (18%).

(2) The period of time necessary for water under definite conditions to pass through the leather. For this purpose use may be made of a very simple apparatus, consisting of an open metallic cylinder about 60 cm. high, to the lower end of which a disc of the leather may be fitted tight by means of a ring with pressure screws. The leather should be placed with the bloom towards the inside of the cylinder and its thickness should first be measured. The cylinder is filled with distilled water to a height of 50 cm. and left suspended until water passes through the leather and begins to drip. In expressing the result, the time necessary is given and also the thickness of the leather.

5. Microscopical Examination. In some cases this may give useful indications and is carried out either with reflected light and moderate magnification for the purpose of observing the characteristic grain and any defects, or with transmitted light, a piece of the leather hardened in methyl alcohol being cut into very thin sections with a razor. These sections may be stained by immersion for 24 hours in dilute picrocarmine solution and are then observed in aqueous glycerine. With well tanned leather, dark, shining masses are seen in the interstices between the fibres ; by picrocarmine the fibres are coloured canary-yellow and the connective tissue and cellular nuclei red. In every case it is well to make the microscopic examination in comparison with samples of known quality.

2. Chemical Analysis

The principal determinations to be made on leather are those of moisture, ash, fatty substances, substances soluble in water (tannins and non-tannins) and nitrogenous substances (hide substances) ; from the results it is then possible to calculate the combined tanning substances and the true leather substances, also the leather yield and the degree of tannage. Other determinations which may be required are those of the sugars, free sulphuric acid and lime (in the ash).

The components are usually calculated on a normal percentage of moisture (18% for **unstuffed leathers**: *see* later). In some cases the results have to be calculated on the dry matter and for stuffed leather sometimes on the dry fat-free material.

The methods used are as follows.

1. Moisture.—5–10 grams of the finely divided leather are dried at 100–105° to constant weight and the percentage loss calculated.

With stuffed leather, an error is introduced owing to the oxidation which some fats undergo on prolonged heating in contact with the air : in such cases

if rigorously exact results are required, the drying must be carried out in a vacuum or in a current of carbon dioxide.

2. Ash.—5–10 grams of the substance are carefully charred in a dish and then calcined at dull redness with addition of a little ammonium nitrate to facilitate the combustion. With this method complete incineration is often difficult ; in such a case it is preferable to weigh the leather in small pieces and to throw it, piece by piece, into a crucible heated to dull redness, each piece being added only after the previous one has burnt away completely.

With a large amount of ash, it is well to make a qualitative analysis. The ash of true leather tanned with tannin consists essentially of calcium carbonate with traces of iron and of phosphates. Coloured leathers may contain metals from the mordants used (tin, copper, iron, chromium, aluminium) ; tin may also be introduced as stannous chloride used for bleaching. Small quantities of silicates (talc, kaolin) may be employed in the treatment of the leather. Finally, other mineral matters (barium, magnesium and lead salts and sodium chloride) may have been added as filling to increase the weight. Complete quantitative analysis of the ash is rarely necessary, but determination of its *calcium* content is sometimes required, this being made by the ordinary methods.
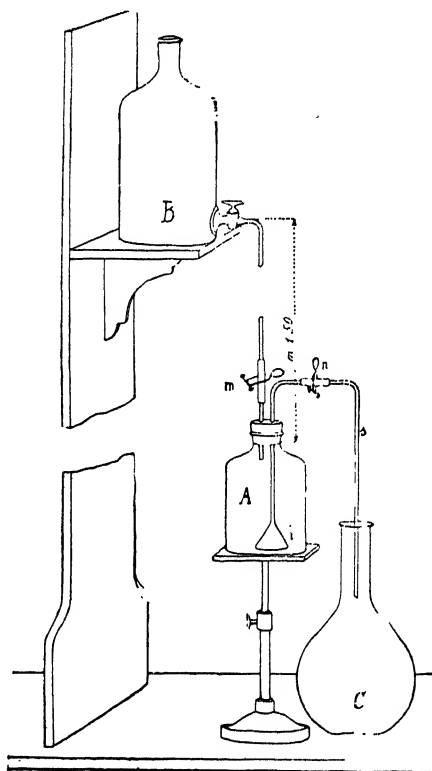
FIG. 66

3. Fatty Substances.—20 grams of the finely divided or powdered leather are extracted in an extraction apparatus with carbon disulphide or petroleum ether ; at the end of the extraction the bulk of the solvent is distilled off and the residue evaporated in a tared dish on a water-bath and dried at 100–105° to constant weight.

Some substances, such as dégras, are not, however, dissolved completely by solvents.

If the fatty substances are considerable in amount, their constants are determined to ascertain their nature (*see* Fatty Substances, Vol. I).

4. Soluble Substances.—The fat-free leather from the preceding determination is dried in the air to expel the solvent, then left for 12 hours in contact with about 200 c.c. of water at the ordinary temperature, and afterwards extracted for 1·5–2 hours with further quantities of water up to a volume of a litre. This may be effected by a displacement apparatus,

such as Koch's (Fig. 66), consisting of a wide-necked bottle A of about 200 c.c. capacity, closed with a stopper through which pass (1) a glass tube reaching just below the stopper and passing above the stopper through a rubber joint and clip m to the side-tube of the bottle B of water about 1·5 metres above, and (2) a second glass tube expanded to a funnel i near the bottom of the bottle A and joined outside through a clip n to a siphon tube s dipping into a litre measuring flask C. The funnel i is closed with gauze or muslin, and the bottle A charged with the material and with water. After 12 hours, the clips m and n are opened, the liquid from A being thus forced into C. The operation is then continued, the velocities of inflow and outflow being regulated so that the volume of a litre is reached in the prescribed time.

The aqueous solution thus obtained is filtered and 200 c.c. (corresponding with 4 grams of the leather) evaporated on a water-bath and the residue dried at 100° : this represents *total soluble matter* or *loss on washing*. The dried residue is then incinerated, the ash representing the *soluble mineral matter* or *soluble ash* (which may be examined qualitatively) ; the difference gives the *soluble organic matter*.

Another quantity of 500 c.c. of the filtered aqueous solution (corresponding with 10 grams of the leather) is concentrated to 125 c.c., in which the *soluble non-tannins* are determined by means of hide powder, as described for tanning substances (*see* p. 340). Subtraction from the result of the amount of the soluble mineral matter gives the *soluble organic non-tannins*.

Finally, the difference between the total soluble matter and the soluble non-tannins gives the soluble tannins or the tannin uncombined with the hide.

5. Hide Substance, combined Tannin and Leather Substance.— The *hide substance*, i.e., the nitrogenous matter constituting the hide, is ascertained from the proportion of nitrogen in the leather,[1] this being determined by the Kjeldahl-Ulsch method (*see* Vol. I : Fertilisers) on 0·6 gram of the finely divided leather ; 100 parts of hide substance contain on the average 17·8 parts of nitrogen in the case of ox-, horse- and pig-skin, 17·4 with goat-, stag- and reindeer-skin, and 17·1 with sheep-skin.

From this result and those of the determinations of sections 1–4, the percentage of *combined tannin* is obtained by subtracting from 100, the sum of the percentages of moisture (taken as 18 if the other components are referred to the substance with normal moisture content), ash, fat, soluble organic substances and hide substance determined as above.

Lastly, the sum of the hide substance and the combined tannin gives the *leather substance* or leather proper.

As a check, the leather substance may be determined directly by weighing the leather remaining from the extraction of the fatty substances and of the soluble matters (*see* above, sections 3 and 4) after pressing and drying at 100–105°, the weight found being calculated for 100 parts of the material (with normal moisture content) and then diminished by the percentage of ash—the latter already diminished by the percentage of soluble ash.

[1] This assumes the absence of other nitrogenous matters, such as glue and the like, which are sometimes added to the leather and are rendered insoluble by the tannin and so increase the weight.

Finally, the *total tannin* is calculated as the sum of the combined tannin, determined as above, and the non-combined determined as in section 4.

6. Calculation of the Leather Yield and of the Degree of Tannage. —The *leather yield* is the weight of leather (with normal moisture content) derived from 100 parts of hide substance. If d is the percentage of the latter (referred to the leather with normal moisture content), the leather yield is given by $10000 \div d$.

The *degree of tannage* indicates the tannin combined with 100 parts of hide substance; if t is the percentage of combined tannin, the degree of tannage is expressed by $100\ t \div d$.

7. Sugars.—These are determined more especially when the soluble organic matter is high and particularly when the non-tannins in it are greater in amount than the tannins and thus raise suspicions as to adulteration with sugars or materials containing them, e.g., dextrin syrups, maltol, etc.

For this determination use may be made of an aqueous solution prepared as for the determination of soluble substances (20 grams of the leather with a litre of water). Such aliquot part of this is taken as, when concentrated and made up to 200 c.c., gives a solution containing not more than 1% of sugar; as a rule 800 c.c. are required. The 200 c.c. of solution are shaken with 20 c.c. of basic lead acetate solution, left for a quarter of an hour and then filtered through a dry filter; to 100 c.c. of the filtrate (which should give no further precipitate with the lead acetate) are added 100 c.c. of sodium sulphate solution of concentration corresponding with that of the lead acetate, the liquid being shaken, allowed to settle and again filtered. The filtrate is used for the determination of the reducing substances [1] by means of Fehling's solution—either gravimetrically or volumetrically (*see* Sugars, General Methods, pp. 109 and 112).[2]

If saccharose (molasses) is present, this may be determined by inverting another part of the filtered liquid after treatment with sodium sulphate and determining again the reducing sugars with Fehling's solution: increase in amount of invert sugar, multiplied by 0·95, gives the saccharose.

When all that is required is to ascertain if the leather contains more than a given quantity of reducing substances (e.g., 1·5 or 2%), the following test may be applied: 30 grams of the leather are exhausted with hot water, filtering through a cloth and washing and pressing the leather; the solution is concentrated, treated with the necessary amount of basic lead acetate and then with sodium sulphate to complete precipitation, made up to 100 c.c. and filtered. If 10 c.c. of Fehling's solution (diluted with 40 c.c. of

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[1] The reducing substances, which may be glucose, maltose, etc., are calculated as glucose.

The presence of glucose may be due also to addition of dextrin syrup; in this case the rotation of the filtered liquid will be greater than that calculated for the glucose found (*see* chapter on Sugars).

[2] If the glucose alone is to be determined, a lesser quantity of the solution is sufficient. Thus, 400 c.c. of the original solution may be concentrated and made up to 100 c.c., treated with 10 c.c. of basic lead acetate and filtered; 50 c.c. of the filtrate are treated with 5 c.c. of sodium sulphate solution and the liquid refiltered and used for the test with Fehling's solution.

water) are reduced completely by 11 c.c. of the filtrate, the leather contains more than 1·5% of reducing substances, and if 8·25 c.c. of the filtrate are sufficient, more than 2% of reducing substance are present.

8. Free Sulphuric Acid.—This determination presents much difficulty and uncertainty since, besides any sulphuric acid used in the preparation of the leather and neutral sulphates which may be present, sulphuric acid may be formed either from the sulphur of the hide substances, or from colouring matters containing sulphur or from sulphured oils or fats. For determining the free sulphuric acid the following methods have been suggested:

(*a*) BALLAND AND MALJEAN'S METHOD. This consists in determining the total and combined sulphuric acid, the free acid being given by difference. To estimate the total sulphuric acid, 10 grams of the leather are moistened in a platinum dish with 10 c.c. of 10% sodium carbonate solution and with a little potassium nitrate. The mass is dried at a gentle heat and cautiously incinerated, the residue being taken up in hot water with addition of bromine water and hydrochloric acid. The liquid is filtered, the residue washed with water and the sulphuric acid determined in the filtrate as $BaSO_4$ and calculated as SO_3. The combined sulphuric acid is determined by incinerating another 10 grams of the leather without addition of soda and nitre, the procedure being as before.

The difference between these two amounts (as SO_3) is diminished by 0·14% (referred to leather with the normal amount of moisture), this being the mean quantity of SO_3 formed, during the determination of the total sulphuric acid, by the oxidation of the sulphur in the hide substance. It scarcely needs mention that, when aluminium, chromium and ferric sulphates are present, these lose sulphuric anhydride during the determination of the combined sulphuric acid and are converted into oxides. To obtain exact results in this case, it is necessary to ignite strongly to complete decomposition of these sulphates, to estimate the three oxides in the ash and to subtract from the resultant free sulphuric acid also the SO_3 corresponding with the oxides thus found.

This method, although often recommended, is not free from inconveniences, besides being excessively long and complicated.

(*b*) F. JEAN'S METHOD. A weighed quantity of the leather is extracted in an extraction apparatus with absolute alcohol to which is added a little sodium carbonate to neutralise the acid. The alcohol is then distilled off, and the residue taken to dryness, taken up again in water and hydrochloric acid and precipitated with barium chloride, the result being calculated as SO_3.[1]

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Good tanned leather should be of uniform and normal colour in accordance with the quality of the tanning material used; it should exhibit a smooth,

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[1] According to Nicolardot (*Ann. des Falsifications*, 1914, VII, p. 195), the free sulphuric acid may be extracted also by boiling with water. In such case it is advisable to operate in presence of barium carbonate: the insoluble residue is treated with hydrochloric acid, the barium sulphate which remains undissolved and corresponds with the free sulphuric acid being weighed.

TABLE XXXIX

Compositions of Various Sole Leathers

Quality.	Mois-ture.	Ash.	Fats.	Soluble Substances.			Leather Substance.			Substances reducing Fehling's Solution.	Leather Yield.	Degree of Tannage.	Author.
				Tanning.	Non-tanning.	Total.	Hide Substance.	Combined Tannin.	Total.				
English, tanned without extract	17·08	0·59	0·84	—	—	20·00	35·37	26·40	61·77	—	—	74·6	Parker
Do.	16·80	0·72	0·92	—	—	18·40	34·90	28·70	63·60	—	—	82·2	Do.
English (West), do.	17·22	0·86	1·09	—	—	20·20	35·00	26·32	61·32	—	—	75·2	Do.
French do.	18·08	0·76	0·11	—	—	7·28	42·60	31·73	74·33	—	—	74·4	Do.
Do do. (pure oak)	18·60	0·58	0·42	—	—	7·04	43·20	30·62	73·82	—	—	70·9	Do.
English, mixed tanning	15·60	1·02	0·80	—	—	16·60	35·60	31·10	66·70	—	—	87·3	Do.
Do.	16·52	0·99	1·10	—	—	18·20	34·70	29·20	63·90	—	—	84·1	Do.
Do.	16·80	0·85	0·90	—	—	18·85	36·10	27·10	63·20	—	—	75·0	Do.
Do.	14·12	0·94	0·81	—	—	22·92	37·30	24·65	61·95	—	—	66·0	Do.
French do.	15·80	1·40	1·40	—	—	18·10	36·00	28·48	64·48	—	—	79·1	Do.
Do.	16·45	1·62	1·10	—	—	17·80	35·60	28·90	64·50	—	—	88·1	Do.
Do.	16·34	1·31	0·95	—	—	17·50	39·20	25·80	65·00	—	—	65·8	Do.
Pure oak tanning	18·00	0·33-0·74	0·13-1·34	1·94-5·01	1·16-4·22	—	41·74-49·02	27·78-32·39	—	0-0·39	204-240	58·1-77·1	Jettmar
German (North)	18·00	0·47-0·73	0·16-0·83	4·56-6·72	2·47-5·12	—	35·68-41·34	30·88-34·26	—	0·16-0·36	242-280	74·8-93·3	Do.
Italian	18·00	0·80	0·50	5·20	1·60	6·80	43·16	30·74	73·90	—	230	71	Baldracco
Do.	18·00	0·77	0·40	8·32	2·29	10·61	40·78	29·44	70·22	0·14	245	72	Do.

shining surface, free from spots, holes or other defects and its section should appear compact, homogeneous and of uniform colour. The specific gravity may vary considerably, but with good sole or belting leather is usually 1–1·1 ; a lower value may indicate faulty preparation, and a high one (sometimes 1·2–1·3) may be caused by addition of extraneous substances (weighting).

The *tensile strength* with sole leather is usually 2–3 kilos per sq. mm. and with good belting leather should be at least 3 kilos ; in the latter case, the less the elongation on tension the higher the quality. The leather should not change or crack when bent to a curve with a diameter ten times the thickness.

Well tanned leathers *absorb water* only in small amount, whereas those of poor quality sometimes absorb much more than their own weight. Further, the less the penetrability, the better the leather.

As regards *chemical composition*, the mean or normal moisture content in unstuffed leather may be taken as 18% with a variation of $\pm 2\cdot5\%$ according to the atmospheric conditions. The mean moisture content a of fatted leathers is given by the formula :

$$a = \frac{8200 + 18\,(100 - g)}{1800\,(100 - g)},$$

where g is the percentage of fat in the dry substance ; the variations may be $\pm 2\%$.

The quantity of *ash* in genuine leathers varies from 0·3 to 2%, the mean being about 1%. When the percentage approaches 2 (1·5–2), the incomplete removal of the lime during the preparation of the hide is suspected, or the use of mineral substances in the dressing of the hide ; an amount exceeding 2% indicates undoubted adulteration (weighting) with mineral matter. These conclusions may be confirmed by the composition of the ash ; as regards lime, this seldom exceeds 0·25% in well prepared leather, but may be as high as 0·5% if the hide has been delimed by means of sulphuric acid.

Fatty substances are usually present in unstuffed leathers to the extent of 0·2–1% or, at the most, 1·5%, except with certain hides, such as those of the sheep and boar, in which 3–6% may occur. Lightly oiled leathers may contain about 3% of fats, and those greased, for belting and boot-uppers, contain fat in varying quantity, which may reach and even exceed 30–35%.

Substances soluble in water may be present in varying quantity according to the quality of the leather and the process of tanning adopted, and great disparity of opinion exists as to the maximum amount to be allowed in a good leather. In genuine leathers, however, the soluble tanning substances are at least equal and often greatly superior in amount to the non-tannins ; the latter should be almost entirely organic and should contain no sugars, with the exception of a very small quantity of reducing substances derived from the tanning materials used (usually about 0·25%, but generally 1·5–2% is allowed).[1]

The percentages of *hide substance* and of *combined tannin* vary greatly according to the quality of the leather and the method of tanning ; in general sole leather contains 60–75% of leather substance, in which the combined tannin is always in smaller quantity than the hide substance, the degree of tannage being less and often considerably less than 100.

The content of *free sulphuric acid* is most important, owing to the harmful effects it may exert on the strength and keeping properties of the leather and of articles made from it. A genuine leather should contain not more than minimal traces of free sulphuric acid ; a small amount is, however, allowable (0·1% according to some and 0·3% according to other authorities). In view of the uncertainty of the methods given for this determination, the limits fixed are of value only when the analytical method to be followed is fixed.

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[1] It should be borne in mind that this permissible amount of reducing substances, if they are really sugars such as glucose, may be an indication of the presence of larger quantities of dextrin.

Table XXXIX on p. 362 gives the compositions of various genuine sole leathers.

CHROMED LEATHER

1. Physical and Mechanical Tests

The external characters (colour and appearance of the surface and section) are examined and determinations made of the specific gravity, strength and permeability as for bark-tanned leather.

2. Chemical Analysis

The analysis of chromed leather comprises the following determinations.

1. Moisture.—As in tanned leather.

2. Ash.—As in tanned leather, but with a smaller quantity of substance. The result obtained does not give the true proportion of mineral matter, since the acids combined with the chromium and aluminium oxides are eliminated during calcination.

Qualitative analysis of the ash will reveal any addition of extraneous mineral substances (weighting).

3. Determination of Chromic Oxide and Aluminium.—A weighed quantity of the substance (2–5 grams) is incinerated in a spacious platinum crucible. The ash obtained is mixed carefully, in the crucible, with about ten times its weight of a mixture of dry sodium carbonate (2 parts) and potassium nitrate (1 part) or of sodium carbonate (15 parts), potassium carbonate (5 parts) and potassium chlorate (1 part), the mass being heated in the covered crucible, at first over a small flame and then for 15 minutes in the blow-pipe flame. When cold the mass is taken up in boiling water, filtered and made up to 250 c.c.

In 100 c.c. of this solution the chromic acid is reduced by prolonged boiling with hydrochloric acid and a little alcohol, chromium and aluminium hydroxides being then precipitated by means of ammonia and the precipitate weighed ($Cr_2O_3 + Al_2O_3$) in the usual way.

Another 100 c.c. of the solution is treated with 5–10 c.c. of concentrated hydrochloric acid and 10 c.c. of potassium iodide solution, the iodine liberated being titrated with standard sodium thiosulphate solution in presence of starch paste and from the result the *chromium oxide* calculated. The *alumina* is then obtained by difference from the two determinations.

4. Fatty Substances and Free Sulphur.—The fats are determined as with tanned leather, carbon disulphide free from sulphur being used for the extraction. If the leather contains free sulphur, this occurs with the fat thus extracted. In such case, when the extracted matter is weighed, it is carefully oxidised in a platinum dish with fuming nitric acid to complete solution; the acid is then evaporated off on a water-bath, the residue neutralised with concentrated sodium carbonate solution, the liquid taken to dryness and the residue ignited. This residue is dissolved in water, the solution acidified with hydrochloric acid, the oxidation completed by boiling with a little bromine water, and the sulphate precipitated with barium chloride. The amount of *sulphur* corresponding with the

barium sulphate found is to be subtracted from the weight of the *fatty matter* obtained as above.

5. Alkali and Total Sulphuric Acid.—The fat-free leather from the preceding operation is dried and weighed, and an aliquot part of it (about 5 grams) treated with 50 c.c. of fuming nitric acid at the ordinary temperature until completely dissolved, this requiring 12–24 hours ; if necessary, the dissolution may be accelerated by gentle heat towards the end of the reaction. The greater part of the acid is then evaporated off and the residue made up to 500 c.c. with water.

In 200 c.c. of this solution the *total sulphuric acid* is determined by precipitation as barium sulphate, the result being calculated as SO_3 ; the value thus obtained includes the sulphuric acid from the free sulphur and that from the sulphur of the hide substance.

To determine the *alkalies*, another 200 c.c. of the liquid are evaporated to dryness, the residue being gently calcined and taken up in water and hydrochloric acid, and the non-alkali metals eliminated by means of ammonia and ammonium carbonate.[1] The filtrate is evaporated to dryness with a little sulphuric acid and the residue heated to expel the ammonium salts and then weighed : this gives the sodium and potassium sulphates together. If required, the two metals may be determined separately (*see* Fertilisers, Vol. I, pp. 124 and 135).

6. Chlorine.—In a platinum dish 3–5 grams of the leather are evaporated to dryness with 25 c.c. of pure 10% sodium carbonate solution, the residue being incinerated and taken up in water ; the solution is neutralised with nitric acid and the chlorine determined by the ordinary gravimetric or volumetric method.

7. Hide Substance.—This is estimated by determining the nitrogen as in tanned leather, 0·5 gram of the substance being taken.

<p style="text-align:center">*
* *</p>

Chromed leather is usually distinguishable from tanned by the bluish-green colour of its surface and section. It has a somewhat lower specific gravity than tanned leather, but is more resistant to tension and bending and to the action of water.

As regards its *chemical composition*, the mean percentage of water is about 15, while the ash often reaches 10–15% and the chromium oxide, 2–5%. The proportion of hide substance is greater than in tanned leather and varies from about 56 to 75%.

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[1] If the qualitative analysis has indicated the presence of magnesia, a little barium hydroxide is added and the precipitate filtered off before the ammonium carbonate is added.

CHAPTER XV

COLOURING MATTERS

The substances used as colours in the arts and industries are of diverse nature and origin ; according to their source and composition they may be divided into two main classes, namely, mineral and organic, these being treated separately below.

MINERAL COLOURS
(Pigments)

These may be *natural* or *artificial*.

Among the former are certain white substances and particularly the *coloured earths*, which consist of earthy or clayey matter exhibiting definite colours owing to the presence of certain metallic compounds (especially of iron) and sometimes of free carbon.

A very important and large group of the artificial colours is that composed of definite metallic compounds (oxides, hydroxides, salts) or of mixtures of two or more compounds, or of carbon either alone or associated with other substances. *Metallic pigments* consist of powdered metals. The *lakes*, formed from organic colouring matters fixed on mineral substances—mostly metallic oxides—are usually considered among the mineral colours.

Pigments are sold either in the solid state in lumps or powder or ready for use, that is, mixed or made into a paste with various materials (*vehicles*) such as water, gum, glue, turpentine, resin or resin oil, fatty oil, etc.

Investigation of these pigments comprises certain technical tests for determining their practical value for the desired purpose and also chemical analysis with the object of identification, determination of the composition and the degree of purity, and detection of adulterants.

Tests to be made similarly for pigments in general—mainly technical tests and certain preliminary chemical tests—are described under the heading General Methods, the separate modes of procedure to be followed with the more important pigments being given later.

GENERAL METHODS
1. Technical Tests

The principal tests necessary to determine if pigments are more or less appropriate to the uses which they should serve in practice are those dealing with the nature and intensity of the tint, covering power, stability towards light, atmospheric agencies, chemical agents and heat, behaviour when

mixed either with other colours or with possible vehicles, behaviour towards the substances constituting the substratum to which it may be applied and, finally, in some cases, the suitability for textile printing.

If the pigment to be examined is already prepared or mixed, it is often necessary first of all to separate it from the medium ; this is effected as described later (*see* Chemical Analysis, No. 1).

1. Tone and Intensity of the Colour.—The tone of a pigment is judged simply by comparing it with other similar materials. The colouring intensity is measured by the more or less intense colour imparted to a given substance by a certain proportion of the pigment and is determined by comparing the material under examination with another chosen as standard. For this purpose, 1 part by weight of the material is intimately mixed with 10 parts of a white substance (zinc oxide, lead sulphate, kaolin, barium sulphate) and the colour compared with that of a similar mixture containing the standard, the two being spread out in proximity on a flat surface. By preparing mixtures of different proportions, the ratio between the colour intensities of the two may be ascertained.

In the case of a white substance, mixtures of this and of a standard white colour with a black (e.g., bone black) or coloured substance in definite proportions are compared. That white is the more intense which, for a mixture of definite proportions, gives the paler colour.

If the substance to be examined is mixed with water or some other material, it must be dried or separated from the extraneous matter before the above test is made.

Finally, with colours for oil painting, it is well to repeat the test by incorporating the necessary quantities of boiled linseed oil with the mixtures prepared from the colour under examination and from the standard colour, the paints thus obtained being spread on a sheet of glass and the colours compared when dry.

2. Covering Power.—This is the power of a pigment, when applied with a suitable medium to a substrate of different colour, to conceal (cover) the latter ; the less the amount of the substance required to cover well a certain area of the substrate, the greater the covering power. This property must not be confused with colouring intensity, since matters with intense colours may have slight covering power, so that when applied as described above they form more or less transparent coatings and allow the colour of the substratum to be recognised.

The covering power may be determined by mixing equal weights of the pigment under examination and of a standard pigment with the necessary quantities of linseed oil, also weighed, and applying the two uniformly with a brush to surfaces of equal area (e.g., a glass or metal plate or a board or plaster surface, white for a dark colour or black for a pale one) until the colour of the surface is covered well and equally in the two cases. The loss in weight of the vessel containing the paint and the brush, together with the known proportion between oil and colour, gives the quantity of the latter used in each case. The larger the scale on which the test is made, the more reliable the results obtained.

Useful indications as to the covering power of pigments may also be

obtained by determining the specific gravity (with the picnometer) and the fineness (by sieving or better by shaking with a liquid, using, for instance, Chancel's sulphurimeter : *see* Vol. I, p. 112), and by microscopic examination.   For one and the same kind of pigment, the covering power becomes greater as the specific gravity diminishes and as the fineness increases and is greater if the structure is amorphous than if crystalline.

With some pigments the *transparency*, that is, the inverse of the covering power, may be required.   This is judged by the same tests as are indicated above for covering power, or better by spreading the pigment, suitably diluted with oil or gum, on a sheet of glass and placing the latter when dry on a white paper with sharp black lines marked on it with Indian ink.   The greater the transparency the clearer will the lines appear.

3. Fastness to Light and Atmospheric Agents.—These tests also are carried out in comparison with a standard colour.   The stability towards light is tested on the pigment either alone or mixed with a medium (gum solution, linseed oil, or something else according to circumstances) which has no action on it (*see* later, paragraph 7).   A certain quantity of the pigment under examination and as much of the standard are spread near one another on wood or other material ;   where mixed colour is used for the test, it is first allowed to dry in a dark place.   The two test surfaces, protected by a sheet of glass and half covered with a black card, are then exposed to a bright light (preferably direct sunlight), observations being made from time to time of the changes in colour undergone by the part of the colour exposed to the light, in comparison with the covered part and also with the standard.   In some cases alteration is detectable after one or several days, but often the lapse of weeks and sometimes of months or years is necessary.   In ordinary cases it is sufficient to ascertain if the tint has altered, and if so to what extent, after a predetermined time chosen for each pigment as a result of experience.

The test of stability towards atmospheric agents is more uncertain, since the possible causes influencing the pigment—action of the air, moisture, variations of temperature, etc.—are very variable.   An approximate criterion of such actions as a whole may be obtained by exposing a certain amount of the pigment and an equal amount of the standard to the air in a place which is covered and feebly illuminated but communicates with the air and is not subject to extraneous gaseous emanations ;   observations are made from time to time to ascertain if the pigment undergoes changes in comparison either with the standard or with the same pigment kept in a full, tightly closed vessel.

4. Fastness to Chemical Agents.—The tests here required vary with the nature of the pigment and the uses to which it is to be put.   Among the more common are tests of stability towards :

(*a*) *Lime* : this is carried out with colours to be used for frescoes.   If the pigment does not change in tone or dissolve when mixed with a paste of slaked lime, it is stable to lime ; to be utilisable in this way, however, the colour must, after drying, be stable to light and atmospheric agencies.

(*b*) *Alkali* : 1 gram of the material is shaken with 10 c.c. of normal

sodium hydroxide solution and left for six hours at the ordinary temperature to ascertain if the colour undergoes change.

Sometimes it is necessary to test the action of gaseous ammonia, the pigment being then left for a definite time in air saturated with ammonia.

(c) *Acids* : the action of more or less dilute acid solutions is sometimes tested, but more often that of acid vapours, particularly of those gases which may easily occur in the air of populous places and works, such as hydrogen sulphide and sulphur dioxide ; these gases, mixed with air, are allowed to act on the pigment in a limited space (e.g., in a box), and any change of colour observed from time to time.

5. Stability to Heating.—This is tested by exposing the pigment to different temperatures according to circumstances and to the uses it is to serve and noting any changes in tint and any fusibility, volatility, etc. This test is especially important with pigments for particular purposes, such as the colouring of sealing-wax, the preparation of fireproof varnish, painting on glass, the decoration of ceramics, etc. ; in these cases it is also well to ascertain the behaviour of the pigment, mixed ready for use, at the temperature at which it is employed.

6. Behaviour towards other Pigments.—Some mineral colours may be mixed to obtain intermediate tints, whereas others cannot be so mixed as reactions would occur altering profoundly their properties and colour. To test if two colours are miscible, they are intimately mixed in a mortar and (if no immediate change occurs) the mixture kept, partly in the light, partly in the dark, and examined from time to time. Change sometimes take place immediately or after a short time, and sometimes only after some years ; if the mixture is heated with a little water, the reactions occur rapidly.

It is often necessary also to test the miscibility of pigments in presence of the medium with which they are to be used ; for this purpose, part of the mixture is mixed with the medium and then spread out on a suitable surface and observed from time to time.

It should be borne in mind that alteration of a pigment in presence of another may be due to impurities (especially soluble salts) contained in one of the two colours.

7. Behaviour towards Media.—Substances with which pigments may be mixed to prepare them for use are somewhat varied. Mention may be made of : water and aqueous solutions of gum, glue, dextrin, and sometimes of albumin, sugars (glucose), glycerine, gum tragacanth, agar-agar or caseinate of lime ; linseed and other drying oils, sometimes with addition of waxes ; fat and resin soaps ; oil of turpentine and other essential oils, mineral, resin and tar oils, alcohol and solutions of resins and balsams.

In order that a pigment may be used with certain media and thus employed for a particular kind of painting, it must be insoluble in these media and must not undergo any chemical or other change in contact with them. The following tests are made :

(a) The pigment is well mixed with the medium in such proportion as to form a dense, homogeneous paste, any changes occurring being noted ; further, a little of the mixture is poured on to absorbent paper and when

A.C. II.   24

the liquid has diffused into the paper the edge of the liquid spot is examined to see if it is coloured, as this would indicate that the pigment is partly dissolved.

(b) The mixture is spread with a brush on a suitable surface, allowed to dry and examined from time to time to see if any changes in colour occur.

8. Behaviour towards the Substratum.—Alteration of pigments by the agency of the substratum, such as paper, cloth, wood, stone or metal, to which they are applied is rare. Examination should, however, be made of the behaviour of the pigments prepared with different media towards the substratum, as regards adherence, any physical alterations of the surface produced by unequal expansion and other similar inconveniences, these depending on the medium and on the preparation of the surface of the substratum more often than on the nature of the pigment used.

9. Printing Test.—This test is made with pigments for textile printing in comparison with a standard pigment, and is carried out as follows : 25–100 grams of the pigment are thoroughly mixed with 25 grams of zinc white paste (500 grams of zinc oxide per litre), 15 grams of water, 15 grams of glycerine, 15 grams of gum solution (1000 grams per litre of water), 150 grams of albumin solution (1000 grams per litre of water) and 3 c.c. of olive oil. The mixture is sieved and used for printing a piece of cotton material, which is then steamed for an hour and afterwards washed and compared with similar printing made with the standard pigment.

2. Chemical Analysis

If the pigment is prepared for use, the medium should first be separated and identified, as described in paragraph 1. The qualitative and quantitative analysis of the colour is treated in general in paragraphs 2 and 3.

1. Detection and Separation of Media.—Part of the pigment is heated to redness on platinum foil to ascertain if fumes are evolved, if charring occurs and what odour is emitted. From the odour it is easy to detect glue, gum, fat or resin.

Another part of the pigment is heated with water and filtered, the filtrate being evaporated to dryness and the residue tested for glue and gum.

Another portion is shaken with ether and filtered, the filtrate being evaporated and the residue examined for fatty oils, resin, turpentine, etc.

The presence of extraneous substances and their nature being thus recognised, these are separated as far as possible from the pigment by means of solvents.

If these substances are soluble in water, a weighed quantity of the product is extracted several times with hot water and filtered each time, the insoluble part being finally washed, dried and weighed ; this constitutes the pigment itself. Under this treatment, however, certain components or impurities of the pigment may pass into solution, whilst sometimes traces of soluble substances are held tenaciously by the insoluble part.

In the case of substances soluble in ether, as with oil colours, a weighed quantity (20–50 grams) of the product is well shaken in a tared flask with 200–300 c.c. of ether and allowed to settle, the ethereal liquid being decanted

on to a tared filter and the insoluble residue remaining in the flask treated with a further quantity of ether ; th's procedure is continued until a few c.c. of the final ethereal liquid leave no residue on evaporation. The ether remaining in the flask is allowed to evaporate at the ordinary temperature and the flask and filter dried together at about 40° and reweighed : the weight of the pigment is thus obtained.

This remaining pigment often, however, contains small quantities of oil, either saponified or oxidised. These may be removed by means of dilute alcoholic caustic potash, when this is without action on the colour, or the oxidised fatty acids may be extracted with phenol, which readily dissolves them and does not act on mineral colours. On the other hand, small quantities of certain pigments may pass into the ethereal solution in combination with the fatty acids ; these may be separated by shaking the ethereal liquid with an appropriate acid, in which the mineral substances are then sought.

After extraction with ether as described above, the pigment should be thoroughly mixed in a mortar before examining it, since with mixtures the heavier components are deposited in the ether before the lighter ones, so that strata of different compositions are formed. In some cases this is recognised by the appearance of the deposit and useful indications on the nature of the mixture may be thus obtained : e.g., when a coloured and a white substance are mixed, or two coloured ones (for instance, chrome yellow and Prussian blue).

2. Qualitative Tests.—Natural mineral colours are usually mixtures of various components in different proportions, whereas artificial ones mostly have definite compositions. Qualitative analysis is made with the object of ascertaining the composition and thus the nature of the pigment and of detecting impurities and adulterants ; to this end the general procedure of inorganic analysis may be followed or, more simply, certain tests and reactions suited to each particular case may be carried out.

As regards *impurities*, coloured earths may contain extraneous substances naturally, while in artificial colours may be found substances derived from the raw materials or from the processes of manufacture, that is, with products which are only required technically, and not absolutely, pure. It is, however, essential that the impurities should not be harmful under the conditions in which the pigment is to be used.

As regards *adulteration*, tests should be made to ascertain if the pigment is substituted by or mixed with others less expensive or with substances which increase its weight, or with small proportions of other pigments with the object of improving or enhancing its colour.

The last purpose is sometimes attained by addition of mineral colours (e.g., a white with a tendency to yellow is mixed with a small quantity of a blue to make it appear pure white), but more often by means of artificial organic dyes which give very bright colours even in small proportions but are only slightly stable and alter more or less as time passes. The recognition of the latter is thus important and is effected by heating separate portions of the colour with water, alcohol and ether and filtering the solutions. If any of the filtrates is coloured, an artificial organic colouring

matter is present; this may then be identified by the tests given later for such colours.

Some artificial organic colouring matters, in the form of lakes, may be insoluble in the above solvents: in such cases they are identified after decomposition of the lake with alkali or acid.

3. Quantitative Analysis.—This comprises determinations of the essential components on which the purity and value of the pigment depend, and determinations of any impurities and adulterants. The determinations to be made with the separate colours are given below.

SPECIAL PART

White Pigments

The mineral substances mainly used as white pigments are: *Lead carbonate (white lead), lead sulphate, zinc oxide (zinc white), zinc sulphide* mixed with *barium sulphate*, these being obtained artificially; artificial (*fixed white*) or natural *barium sulphate*, natural or artificial *calcium carbonate* (*chalk*), natural or artificial *calcium sulphate* (*gypsum*).

More rarely use as white pigments is made of other substances, such as bismuth subnitrate, antimony oxide and oxychloride. Many other white substances insoluble in water could be used similarly, such as kaolin, talc, silica, bone ash, etc., but these are not generally used as they are less suitable or less convenient than those indicated above, or they are only used in certain cases to mix with other colours.

The complete analysis of each of the more important white pigments is described below. The following scheme (Table XL) of reactions serves for the ready differentiation of the various whites (when not mixed), without following the general procedure of qualitative analysis.

WHITE LEAD

This consists of a basic carbonate, corresponding in composition approximately with the formula, $2PbCO_3$, $Pb(OH)_2$. It may contain various impurities resulting from the manufacture, especially basic lead acetate and it may be adulterated with barium sulphate, lead sulphate, zinc white, bone-ash, witherite, gypsum, chalk or clay (kaolin). Mixtures of white lead with barium sulphate are given special names, e.g.: *Venetian white* (equal weights of white lead and barium sulphate), *Hamburg white* (1 part of white lead to 2 parts of barium sulphate), *Dutch white* (1 part of white lead to 3 parts of barium sulphate). White lead mixed with gum and moulded into cakes is termed *Krem's white*.

Analysis of white lead includes, besides technical tests (*see* General Methods), qualitative examination for the detection of impurities and adulterants (*see* paragraph 1) and certain quantitative determinations (*see* succeeding paragraphs).

Table XL

Systematic Scheme for the Recognition of White Pigments

With hydrochloric acid

gas liberated

— **carbon dioxide**
- substance soluble in the hot; on cooling lead chloride crystallises—more easily soluble in nitric acid—the acid solutions, neutralised with caustic soda and re-acidified with acetic acid, give a yellow precipitate with potassium chromate—the substance blackens with hydrogen sulphide or ammonium sulphide; on heating it becomes yellow . . *White lead*
- substance easily soluble in the cold; the same with nitric acid—the solutions give a white precipitate with ammonia and ammonium oxalate . . . . *Chalk*

— hydrogen sulphide—substance only partially soluble; the filtrate, neutralised with soda and re-acidified with acetic acid, gives a white precipitate with hydrogen sulphide . *Lithopone*

soluble without evolution of gas
- soluble easily in the cold; the same with nitric acid—the acid solutions, neutralised with soda and re-acidified with acetic acid, give a white precipitate with hydrogen sulphide —the substance is insoluble in sodium hydroxide; on calcination it turns yellow and becomes white again on cooling. . . *Zinc white*
- soluble in the hot; the solution gives a white precipitate with ammonia and ammonium oxalate and a white precipitate with barium chloride . . . . *Calcium sulphate*

insoluble or almost so; the same with nitric acid
- substance soluble in hot ammonium acetate solution; with potassium chromate the solution gives a yellow precipitate . . . *Lead sulphate*
- substance insoluble in ammonium acetate—when heated on charcoal in a blowpipe flame and then treated with hydrochloric acid, it yields hydrogen sulphide and gives a solution which colours the flame green . . . . *Barium sulphate*

1. Qualitative Examination.—A few grams of the substance are treated repeatedly with boiling water and filtered: the solution may contain lead acetate and calcium sulphate (if both are present, however, soluble calcium acetate and insoluble lead sulphate are formed). In the solution lead is tested for with hydrogen sulphide, calcium (after elimination of the lead) with ammonia and ammonium oxalate, and sulphuric acid with barium chloride. Acetic acid may be detected in a separate portion of the substance by moistening it with sulphuric acid and a few drops of alcohol and heating gently: in presence of acetates, the odour of ethyl acetate is observed.

The residue insoluble in water is treated with excess of dilute nitric

acid and the solution, filtered if necessary, evaporated to dryness with sulphuric acid ; the residue is taken up in water, the lead sulphate formed allowed to settle and the liquid filtered. In the filtrate, neutralised with soda and acidified with acetic acid, any zinc present is precipitated with hydrogen sulphide and, after filtration, the calcium phosphate with ammonium chloride and ammonia, and the calcium and any barium with ammonium oxalate.

The residue insoluble in nitric acid may contain lead sulphate, barium sulphate and clay (possibly also a little calcium sulphate). The first of these dissolves in the hot in ammonium acetate solution and this solution then gives a yellow precipitate with potassium chromate. The calcium sulphate dissolves in hot, dilute hydrochloric acid. Barium sulphate may be recognised, after reduction on charcoal in the blowpipe flame, by treating with hydrochloric acid and noting the green coloration of the flame. Finally, clay is recognised by fusing a little of the residue with sodium carbonate and taking up in hydrochloric acid : the silica is thus separated and the aluminium passes into the solution.

2. Determination of the Hygroscopic Water.—About 10 grams of the substance are dried at 100° to constant weight.

3. Loss on Calcination.—From 2 to 3 grams of the substance are heated to dull redness in a porcelain crucible to constant weight. The loss of weight represents carbon dioxide plus hygroscopic and combined water ; the latter may be obtained by difference.

4. Carbon Dioxide.—This is determined by one of the methods described for chalk (*see* Vol. I, p. 139), dilute nitric acid being preferably used for the action.

5. Insoluble Substances.—5 grams of the substance are treated in the hot with 40 c.c. of pure nitric acid, about 40 c.c. of water being then added and the liquid boiled and left to settle. The clear liquid is decanted through a filter on which the insoluble matter is collected, well washed, dried at 100–105°, calcined and weighed. The weight of the residue, multiplied by 20, gives the percentage of insoluble residue in the white lead.

It is rarely necessary to determine quantitatively the separate components of the residue. When the lead sulphate is to be determined, the residue is extracted with ammonium acetate solution in the hot, the liquid filtered and the filtrate precipitated with hydrogen sulphide ; the lead sulphide is dissolved in nitric acid, and the procedure indicated in the next section (6) followed.

6. Soluble Lead.—The nitric acid solution obtained as in the preceding determination, together with the wash waters of the insoluble residue, is made up to a definite volume and an aliquot part, corresponding with about 1 gram of substance, evaporated with 5 c.c. of dilute sulphuric acid first on a water-bath and then on a sand-bath until white fumes of sulphuric acid appear. When cold, the residue is taken up in water containing a little alcohol, the liquid being allowed to settle and filtered, best through a Gooch crucible ; the residual lead sulphate is washed first with water containing a little alcohol and 0·5% of sulphuric acid and then with dilute

alcohol, being afterwards dried, gently calcined and weighed : $PbSO_4 \times$ 0·68311 = Pb or $\times$ 0·73589 = PbO.

If the white lead contains appreciable amounts of calcium compounds, this method is inaccurate since part of the calcium is precipitated together with the lead as sulphate. In such case, the nitric acid solution should first be evaporated, the residue being taken up in water and the lead precipitated as sulphide ; this is collected on a filter, washed and redissolved in nitric acid, the subsequent procedure being as described above.

In the rare cases where it is required to determine, in the filtrate from the lead precipitate, any other components (zinc, calcium, etc.), this is done by the ordinary methods of quantitative analysis.

7. Determination of the Acetic Acid.—A fairly large quantity (up to 100 grams) of the substance is placed in a flask fitted with a funnel tube dipping almost to the bottom and a delivery tube connected with a condenser. Dilute sulphuric acid is added through the funnel, gradually and with shaking, until evolution of carbon dioxide ceases, the liquid being then distilled over until the distillate is neutral. The distillate is tested to make sure that it does not contain sulphuric acid (if it does, it must be redistilled) and is then titrated with N/10-NaOH : 1 c.c. = 0·006003 gram of acetic acid.

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White lead of normal composition should contain theoretically 86·33% of PbO, 11·35% of CO_2 and 2·32% of H_2O. Commercial white leads usually contain 83·5–87% PbO, 11–16% CO_2 and 1–2·5% H_2O, but those most valued, especially for their covering power, are the ones poor in carbonate, i.e., containing 85–87% PbO, 11–12% CO_2 and 2–2·5% H_2O ; samples containing more than 14% of CO_2 are mostly of poor quality. Loss on calcination varies from 13 to 16% and with the best products does not usually exceed 14%.

White lead should not be mixed with other white colours and should be free from lead acetate ; according to some authorities, the latter is allowable in amount corresponding with not more than 0·2% of acetic acid.

ZINC WHITE

This consists of zinc oxide in the form of a light, odourless, white powder. It may contain, as impurities, lead carbonate and sulphate and oxides of iron, cadmium and arsenic, and may be adulterated with chalk, barium sulphate and clay (kaolin). Besides the technical tests already described (*see* General Methods), the following tests and determinations are made.

1. Qualitative Examination.—A portion of the substance is moistened with ammonium sulphide : a blackish coloration indicates presence of lead or iron, and a yellow one, cadmium or arsenic. The presence of the latter is best shown by dissolving about 1 gram of the substance in a little concentrated hydrochloric acid and adding 5 c.c. of Bettendorf's reagent (*see* Vol. I, p. 18) : presence of arsenic is manifested by a brown coloration, followed by a black precipitate ; if arsenic is absent, no coloration will be observed even after an hour.

Another portion of the substance is boiled with water and filtered, the

filtrate being tested for sulphuric acid by means of barium chloride. A positive reaction indicates the presence of calcium sulphate, or possibly zinc sulphate, so that the separate metals must be tested for in the aqueous solution.

The residue insoluble in water or a new portion of the substance is treated with dilute acetic acid, in which the zinc oxide should dissolve easily without evolution of gas. Effervescence indicates carbonates (white lead, chalk) ; if hydrogen sulphide is evolved, zinc sulphide (lithopone) may be present. Any residue insoluble in acetic acid may contain lead, barium or calcium sulphate or clay, these being recognised as in white lead (*q.v.*, paragraph 1). Lastly, the acetic acid solution, when treated with caustic soda, should give a white precipitate quite soluble in excess of alkali and the alkaline solution should give a white precipitate with ammonium sulphide.

2. Moisture.—5 grams of the substance are dried in an oven at 100° to constant weight.

3. Insoluble Matter.—About 5 grams of the substance are treated with dilute nitric acid (or with hydrochloric acid if lead carbonate and calcium sulphate are not present in appreciable proportions) ; the solution is filtered and the insoluble residue washed, dried, calcined and weighed.

If necessary, lead sulphate may be determined in the residue in the way described for white lead (*q.v.*, paragraph 5).

4. Soluble Lead.—The nitric acid solution from the preceding determination is evaporated with a little sulphuric acid first on a water-bath and then on a sand-bath until fumes of sulphuric acid appear. The cold residue is taken up in water and the lead sulphate estimated as with white lead (*q.v.*, paragraph 6). The lead thus found is that corresponding with the white lead contained in the product under examination.

5. Zinc.—The filtrate from the preceding determination, heated to boiling to eliminate the alcohol and acidified with hydrochloric acid (or, in absence of lead, the original acid solution, evaporated to dryness if nitric acid is present and then taken up in water and hydrochloric acid), is treated with a current of hydrogen sulphide to precipitate the cadmium and any other metals of Group II present ; the solution is then filtered and the filtrate, freed from hydrogen sulphide by boiling, made up to a definite volume, an aliquot part of it being then neutralised with caustic soda, acidified with acetic acid and again treated with hydrogen sulphide. The precipitated zinc sulphide thus obtained is washed with hydrogen sulphide solution, dried, calcined with sulphur in a Rose crucible in a current of hydrogen, and weighed : $ZnS \times 0.83507 = ZnO$.

<p style="text-align:center">**</p>

Good *zinc white* should contain not more than 3% of moisture and the remainder should be composed almost entirely of zinc oxide ; it should contain as little as possible of lead carbonate and sulphate and should be free from cadmium, arsenic, iron and insoluble substances.

LITHOPONE

(Griffiths' White)

This is a mixture of zinc sulphide and barium sulphate in the form of a very fine powder, white or slightly grey (in the lower qualities). It may contain, as impurities derived from the raw materials and from the manufacturing processes, zinc oxide, and sometimes carbonate, oxides of iron and lead (rare), alumina, lime, magnesia and small quantities of barium carbonate or sulphide and soluble salts (chlorides, sulphates). It may be adulterated with excess of barium sulphate and also with chalk, gypsum and clay. Its value depends, besides on the absence of such impurities and adulterants, essentially on the proportion of zinc sulphide.

In addition to the technical tests, among which that of the stability towards light is of particular importance, the analysis of lithopone includes qualitative tests for the various extraneous substances mentioned above and the determinations given below.

1. Qualitative Examination.—A portion of the substance is treated with hot water and filtered, the filtrate being tested for chlorides and sulphates. The residue is treated with hydrochloric acid in which it dissolves partially with evolution of hydrogen sulphide; the solution is tested for lead by means of sulphuric acid and any precipitate formed filtered off, the filtrate being neutralised with caustic soda, acidified with acetic acid and the zinc precipitated with hydrogen sulphide. The liquid is then filtered and the filtrate, after being heated to expel hydrogen sulphide, tested for iron, aluminium, calcium, barium and magnesium by the ordinary methods of qualitative analysis.

The part insoluble in hydrochloric acid consists of barium sulphate and may also contain clay, the presence of which may be determined after disaggregation by the ordinary methods.

2. Moisture.—5 grams of the substance are heated in an oven at 100–110° to constant weight.

3. Substances soluble in Water.—The dry substance from the preceding determination is shaken with hot water, filtered through a filter previously dried at 100–110° and tared, and washed until the wash water no longer gives the reactions for chlorides and sulphates; the insoluble residue is then dried at 100–110° and weighed. (Loss of weight) × 20 = percentage of soluble matter.

4. Total Zinc.—The substance remaining from the preceding operation is introduced into a 500 c.c. measuring flask and boiled with 100 c.c. of hydrochloric acid (D 1·12) until the smell of hydrogen sulphide is no longer detectable, the liquid being then cooled, made up to the mark with water, shaken and filtered through a dry filter. The first portion of the filtrate is discarded and of the remainder 100 c.c. (= 1 gram of original substance) are heated to 60–70° with 50 c.c. of water, a little ammonium chloride and excess of ammonia and the zinc precipitated by slight excess of white ammonium sulphide. The zinc sulphide is allowed to settle for some hours, the supernatant liquid being then filtered and the precipitate then also brought

on to the filter, washed with hot water containing a little ammonium sulphide and weighed as sulphide after calcination with sulphur in a current of hydrogen (*see* Zinc White, paragraph 5). In technical determinations, it is sufficiently accurate to calcine the sulphide in the air in a porcelain crucible and weigh as oxide.

If treatment with ammonia gave a flocculent precipitate (ferric or aluminium hydroxide), the weighed zinc oxide is dissolved in dilute hydrochloric acid, the solution treated with ammonium chloride and excess of ammonia, and the precipitate collected, washed, again dissolved in hydrochloric acid and reprecipitated with ammonium chloride and ammonia; the precipitate thus obtained is collected, washed, calcined and weighed. The weight of the ferric oxide and alumina thus obtained is deducted from that of the zinc oxide previously found.

5. Zinc occurring as Oxide.—5 grams of the substance are placed in a 250 c.c. measuring flask with 100 c.c. of dilute acetic acid (50 grams per litre), which in the cold dissolves only the zinc present in the form of oxide (or carbonate). The flask is well shaken for a considerable time, the liquid then made up to the mark with water and filtered and the zinc in 200 c.c. of the filtrate (= 4 grams of original substance) precipitated as sulphide as above.

6. Zinc occurring as Sulphide.—This is calculated by difference from the two preceding determinations. (Zinc oxide corresponding with the total zinc) minus (zinc oxide present as such) = (zinc oxide corresponding with sulphide): $ZnO \times 1 \cdot 19749 = ZnS$.

7. Insoluble Matter (barium sulphate).—The residue insoluble in hydrochloric acid remaining from the determination of the total zinc (paragraph 4) is collected on a filter, washed, dried, calcined and weighed. This weight, if extraneous insoluble substances are absent, represents the barium sulphate.

<p style="text-align:center">**
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Good lithopone should contain not more than traces of soluble salts and impurities, especially ferric oxide, and should not contain added extraneous substances. The proportion of zinc oxide should not be more than 2–3% and the moisture usually amounts to 0·2–0·3%. In some cases, however, zinc oxide is present in considerable amount and moisture to the extent of 1–2%.

The best lithopones are those rich in zinc sulphide and the different qualities are distinguished according to their content of the sulphide. The best contain 32–35% or more of ZnS, and others 29–30%, 25–26%, 22–23%, and the poorest 15–16%. The content of barium sulphate varies from about 60 to 80%.

PERMANENT WHITE
(Constant White)

This consists of precipitated barium sulphate, which is marketed as a fine powder, or more often as a paste containing up to about 30% of water. It is occasionally adulterated with gypsum, chalk and clay.

The technical value is determined by the whiteness and fineness and by making a paste of the white with 2% glue solution and spreading this on a sheet of paper; when dry, the layer should be white, uniform and

adherent and should not become detached when rubbed moderately hard.

The chemical examination of this product is usually limited to a few qualitative tests. A portion is treated with hot dilute hydrochloric acid, and the filtered liquid tested for calcium and sulphuric acid (chalk, gypsum). Another portion is either treated with hot concentrated sulphuric acid or fused with potassium bisulphate ; when cold the mass is treated with water and the solution tested for aluminium.

If the product is a paste the dry matter is determined by washing a weighed quantity with hot water and calcining and weighing the residue.

Red and Yellow Pigments

The principal red and yellow pigments are : *Lead chromate (chrome yellow, orange and red), zinc chromate (zinc or buttercup yellow), barium chromate (lemon yellow or yellow ultramarine)* ; various products based on *ferric oxide, hydrated* (yellow) or *anhydrous* (red), both natural (*yellow* and *red ochres*) and artificial (*Mars yellow, English red,* etc.) ; *red oxide of lead (minium or red lead) ; mercuric sulphide (cinnabar, vermilion) ; antimony oxysulphide (antimony cinnabar) ; cadmium sulphide (cadmium yellow) ; basic lead antimonate (Naples yellow).*

More rarely use is made for the same purpose of other substances such as strontium and calcium chromates, lead oxychloride (Cassel yellow), lead protoxide, arsenic sulphide (orpiment), stannic sulphide (mosaic gold), potassium cobaltinitrite (cobalt yellow), etc.

The principal red and yellow colours (when not mixtures) may be distinguished by the reactions indicated in the scheme on p. 380 ; the following sections treat of the complete examination of the more important of them.

CHROME YELLOW, CHROME RED

These are based on lead chromate and exhibit all gradations in colour from pale yellow to garnet red, but they may be referred to three principal types : *chrome yellow*, normal lead chromate ; *chrome orange*, mixture of normal and basic lead chromates ; *chrome red*, basic lead chromate.

These pigments are often sold mixed with lead sulphate (especially the pale tones), gypsum, barium sulphate, chalk or kaolin.

Their examination includes, besides the technical tests (covering power, tests of stability, etc.), the following tests and determinations.

1. Extraneous Substances (Willenz's method).—1 gram of the substance is treated at a gentle heat with 100 c.c. of dilute hydrochloric acid (1 : 20), which dissolves the calcium salts (gypsum, chalk), effervescence indicating carbonate (chalk) ; the liquid is filtered by decantation and the insoluble part washed, the lime and any sulphuric acid being determined in the filtrate by the ordinary methods.

The part insoluble in dilute acid is digested in the cold with 50 c.c. of ammonium acetate solution (D 1·04), this dissolving the lead sulphate, which may be estimated by evaporating to dryness the filtrate and calcining the residue with a little sulphuric acid.

<div align="center">Table XLI</div>

Systematic Scheme for the Recognition of Red and Yellow Pigments

With boiling hydrochloric acid

soluble with evolution of chlorine; colourless solution, on cooling, lead chloride crystallises—partially soluble in nitric acid leaving a brown residue—the substance blackens with ammonium sulphide . . . . *Minium*

with dilute acid gives a yellow solution; with conc. acid a green solution and evolution of chlorine

  on cooling lead chloride crystallises—soluble in nitric acid, yellow solution—soluble in hot sodium hydroxide to a yellow solution, from which acetic acid brings down a yellow precipitate—the substance blackens with ammonium sulphide . . . . . *Chrome reds and yellows*

  on cooling does not crystallise; soluble in nitric acid to a yellow solution

    the acid solutions are reprecipitated by ammonia and give with sulphuric acid a white precipitate; they colour the flame green—substance insoluble in sodium hydroxide *Baryta yellow*

    the acid solutions are not precipitated by either ammonia or sulphuric acid; when neutralised with soda and re-acidified with acetic acid they give a white precipitate with hydrogen sulphide—substance soluble in hot sodium hydroxide . . . *Zinc yellow*

soluble with evolution of hydrogen sulphide

  the solution, diluted, gives an orange precipitate with hydrogen sulphide—the substance is turned yellowish by alkali and when calcined blackens and emits white fumes . . . . *Antimony cinnabar*

  the solution, diluted, gives a yellow precipitate with hydrogen sulphide—the substance is insoluble in alkali, sometimes becoming more intense in colour . . . . . . *Cadmium yellow*

soluble, often incompletely, without evolution of gas—with nitric acid, ditto—the acid solutions are yellow and give a deep blue precipitate with potassium ferrocyanide—substance insoluble in sodium hydroxide; when ignited it changes from yellow to red and from red to reddish-brown . . . . *Pigments based on ferric oxide*

insoluble or almost so; changes to orange and then to white; by prolonged action of the concentrated acid, lead chloride is formed—with sodium hydroxide the substance changes to orange—when heated on charcoal in the blowpipe flame, it emits white fumes and leaves a brittle metallic globule . . . . *Naples yellow*

insoluble and unalterable; the same also with nitric acid or sodium hydroxide—when heated, volatilises completely and sublimes . . . . *Cinnabar*

The part insoluble in ammonium acetate, containing the lead chromate, barium sulphate and clay, is suspended in 50 c.c. of water, treated with 25 c.c. of caustic potash solution (112 grams per litre) and heated to boiling for 10 minutes ; the lead chromate dissolves, whilst the barium sulphate and clay or kaolin remain undissolved and are collected, calcined and weighed.

2. Normal Lead Chromate.—This may be determined rapidly and, although not rigorously exactly, yet with sufficient approximation for practical purposes, in the following manner : 2·154 grams of the substance are ground in a mortar with a little water and a few c.c. of hydrochloric acid of $D = 1·18$, the whole being poured into a 200 c.c. flask, into which also the mortar is rinsed out with water ; 3–4 grams of pure potassium iodide are then added and the liquid shaken, left at rest for a quarter of an hour, made up to the mark with water, shaken and left for two hours. 100 c.c. of the clear liquid are pipetted off and titrated with N/10-sodium thiosulphate, starch paste being added when the liquid is only faintly yellow and the addition of thiosulphate continued until the blue colour disappears. The number of c.c. of thiosulphate used represents directly the percentage of $PbCrO_4$ in the substance.

3. Excess of Lead Oxide in Chrome Orange and Chrome Red.— 1 gram of the substance is treated in the cold with dilute acetic acid, which dissolves only the lead oxide not combined as normal chromate ; in the filtered solution the lead is estimated by the ordinary methods. When no other substances soluble in acetic acid are present, the insoluble part (normal chromate and any extraneous insoluble substances present) may be collected, washed, dried and weighed ; the lead oxide is then given by difference.

ENGLISH RED, IRON MINIUM

English red consists essentially of anhydrous ferric oxide in very fine powder, more or less deep red in colour. It usually contains small quantities of silica and silicates, alumina, lime and magnesia, and often sulphates, chlorides and free sulphuric acid ; it may also contain manganese and copper. It is often sold mixed with considerable proportions of gypsum (*Venetian red*), barium sulphate and chalk ; sometimes its colour is heightened or modified by addition of artificial organic colours.

The name *Iron minium* is given to a product composed essentially of ferric oxide mixed with clay and sometimes also with siliceous sand and forming a fine, heavy powder of a deep red colour ; this also may be adulterated with gypsum or chalk and may contain admixed organic colouring matter.

The investigation of these products comprises principally technical tests relating to the tone and intensity of the colour and to the covering power, these being carried out by the general methods already described ; sometimes the fineness (by levigation with water) and the specific gravity (with the picnometer, using boiled water) are also determined.

As regards chemical analysis, besides a partial qualitative examination as indicated in paragraph 1 (below), the determinations described in para-

graphs 2–6, especially that of the ferric oxide, may be required. Finally, with these products importance attaches to the resistance to acids (*see* paragraph 7).

1. Qualitative Examination.—A portion of the pigment is treated with a little water and this tested with sensitive litmus paper : an acid reaction indicates the presence of free sulphuric acid. The substance is then boiled with excess of water and filtered, the filtrate being tested for lime and sulphuric acid (gypsum) and chlorides.

Another part of the pigment or the portion insoluble in water is treated with concentrated hydrochloric acid : effervescence indicates carbonates (chalk). When effervescence ceases, the liquid is heated for a long time until the ferric oxide dissolves completely, nitric acid being also added if necessary. The liquid is evaporated to dryness and the residue taken up in hydrochloric acid and hot water and filtered. The insoluble residue is tested by the ordinary methods to see if it consists solely of silica and silicates or if barium sulphate is present.

The acid filtrate is treated with excess of ammonium chloride and with ammonia to precipitate the ferric oxide and any alumina, the precipitate being tested for the latter in the usual way. The filtrate is divided into three parts : one is acidified with acetic acid and tested for copper with ferrocyanide ; in another the manganese (if present) is precipitated with ammonium sulphide, lime and magnesia being then tested for ; in the third sulphates are tested for with barium chloride. Manganese is best sought in a separate portion of the substance by the well-known dry reaction.

The qualitative examination is completed by testing for artificial organic colouring matters by treatment in the hot with alcohol, either alone or in presence of acetic acid or ammonia (*see also* General Methods, p. 371).

2. Insoluble Substances.—From 1 to 2 grams of the pigment are subjected to prolonged heating with concentrated hydrochloric acid, the acid which evaporates being replaced ; this operation is continued until the whole of the ferric oxide is dissolved. Complete dissolution presents some difficulty, especially with products which have been strongly heated ; in such cases it may be hastened by adding a little nitric acid or a few crystals of potassium chlorate. The liquid is ultimately evaporated to dryness and the residue heated in an oven at 110° to render the silica insoluble, treated with hydrochloric acid and hot water and filtered ; the insoluble residue is collected on a filter, washed, dried, calcined and weighed.

3. Ferric Oxide.—The filtrate from the preceding determination is made up, together with the wash water, to a definite volume (e.g., 250 c.c.) and an aliquot part of it (50 or 100 c.c.) precipitated with ammonia in presence of ammonium chloride ; the precipitate is collected on a filter and washed. If alumina is present only in negligible quantity, the weight of the calcined precipitate gives the ferric oxide. In the contrary case, the washed and still wet precipitate is dissolved in dilute sulphuric acid and the solution made up to 100 c.c. with water ; 10 c.c. of this solution are reduced with zinc and the ferrous iron titrated with permanganate (*see* Vol. I, Limestones and Marls, p. 142).

4. Lime.—This is determined in an aliquot part of the filtrate from the

precipitation of the ferric oxide and alumina, by precipitating with ammonium oxalate and then proceeding as usual.

5. Sulphuric Acid.—This is also determined in an aliquot part of the filtrate from the precipitation of the iron and alumina, by acidifying with hydrochloric acid and precipitating with barium chloride in the ordinary way.

6. Copper.—In an aliquot part of the hydrochloric acid solution obtained in determination No. 2 (above) the ferric salts are reduced by means of sodium hypophosphite and the copper then precipitated with hydrogen sulphide, the precipitate being dissolved in nitric acid and the copper then determined electrolytically.

7. Resistance towards Acids.—1 gram of the material is digested with a litre of 1% sulphuric acid with occasional shaking, a few c.c. of the clear liquid being withdrawn every 24 hours and the dissolved iron determined.

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True *English red* should contain only small quantities of impurities (usually not more than 1–2% of substances insoluble in acids) and should consist essentially of ferric oxide ; it should not contain copper or free sulphuric acid. Products containing barium sulphate or chalk or gypsum in other than very small quantities are to be regarded as intentional mixtures ; as much as 80% of gypsum is found in some commercial samples.

Iron minium contains larger amounts of silica and silicates ; it may contain 50–90% of ferric oxide, good qualities containing at least 80% ; it should not contain added extraneous substances.

In general the specific gravity of these pigments increases with the extent to which they have been calcined ; it may vary from 3·8 to 4·5 and in good products is above 4·2. The resistance to acids also increases with the degree of calcination ; good products should not give up more than 1% of ferric oxide to 1% sulphuric acid in 5–6 days. The pigments should not contain artificial organic dyes.

OCHRES

Yellow ochres are earths composed essentially of clay coloured by hydrated ferric oxide ; they may contain siliceous sand, calcium carbonate, small proportions of manganese oxides, and sometimes basic ferric sulphate and calcium and barium sulphates. Chalk, gypsum and heavy spar may be added fraudulently and the colour may be " improved " by artificial organic dyes, vegetable colours or chrome yellow.

Red ochres, which occur naturally but are more often obtained by calcining the yellow forms, are analogous in composition, excepting that the ferric oxide is wholly or partially anhydrous.

An artificial pigment analogous to the ochres is *Mars yellow*, consisting of a mixture of hydrated ferric oxide with calcium sulphate, alumina or zinc oxide ; of analogous composition are the pigments derived from it by more or less pronounced heating (*Mars orange, red, brown, violet, purple*).

Examination of ochres generally includes, besides technical tests of the fineness, the tone and intensity of the colour and the covering power, only certain qualitative tests ; quantitative analysis is rarely required.

1. Qualitative Examination.—This is carried out as with English red and iron minium as far as the detection of calcium sulphate, carbonates, silica, barium sulphate, ferric oxide and alumina, manganese, lime, magnesia, sulphates and artificial organic dyes is concerned.

With yellow ochres, the substance is also tested by heating in a test-tube : the emission of empyreumatic vapours (when organic dyes are not present) shows the presence of humous or bituminous substances and acidity of the water which condenses indicates the presence of basic ferric sulphate.

Yellow ochre may be " improved," besides by artificial organic dyes, also by vegetable colours or by chrome yellow. These are detected by treatment with sodium hydroxide : from the alkaline solution of vegetable colours, the corresponding lakes are precipitated by addition of aluminium sulphate ; the same alkaline solution, acidified with acetic acid, gives a yellow precipitate in presence of chrome yellow.

Some ochres contain arsenic, which may be detected by Marsh's method.

Mars yellow may be distinguished from ochre by qualitative analysis, especially by the tests for calcium sulphate, alumina as such, and zinc oxide.

2. Quantitative Analysis.—This is usually limited to a determination of the ferric oxide, which is carried out as in English red (*q.v.*). In the rare cases when a complete analysis is required, the methods given for clay are applicable (Vol. I, p. 144).

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The *composition of ochres* is very variable : the content of ferric oxide and its degree of hydration, on which the quality and intensity of the colour depend, may vary widely. The colour may be changed to brown (*brown ochres*) by oxides of manganese. A *good ochre* should not contain carbonates or sulphates and should not be adulterated with chalk, gypsum or barium sulphate or " improved " with other colours. Ochres containing arsenic should not be used, especially for internal walls or wall-papers.

MINIUM

This is an oxide of lead with a composition corresponding approximately with the formula Pb_3O_4 (= PbO_2, $2PbO$). It forms a bright scarlet heavy powder with various gradations of colour according to the method of preparation ; a variety with a much paler colour than that of ordinary minium is termed *orange lead.*

Minium may contain various impurities derived from the raw materials of its manufacture, e.g., calcium salts and oxides of iron and copper. It may be adulterated with clay, chalk, gypsum, heavy spar, lead sulphate, brickdust, ochre and other colours with a basis of ferric oxide, and artificial organic dyes.

Mixtures of minium with other colours or with white substances, heightened in colour by artificial organic dyes (usually eosin, cochineal scarlet, crocein, ponceau and the like), or, in some cases, white substances (barium sulphate) coloured with lakes of artificial organic dyes, are often sold as *imitations or substitutes of cinnabar and vermilion.*

In examining minium, some of the technical tests are first carried out.

by the general methods already described, especially those relating to the fineness, the quality and intensity of the colour, the stability towards light and the behaviour towards other pigments (zinc oxide) and also vehicles (oil). The chemical analysis comprises the qualitative tests indicated in paragraph 1 (below) and certain quantitative determinations described in succeeding paragraphs, the most important being those of the extraneous insoluble substances and the lead dioxide.

1. Qualitative Analysis.—The minium is treated with dilute nitric acid; effervescence indicates carbonates; in the solution the lead is precipitated by means of hydrogen sulphide, the filtrate being tested for zinc, iron, aluminium, calcium and magnesium by the ordinary methods. The brown residue insoluble in nitric acid is heated further with nitric acid in presence of either sugar solution or hydrogen peroxide until the lead dioxide is completely dissolved; any insoluble residue then remaining may contain lead sulphate, barium sulphate or clay, which may be identified in the usual way.

The presence of gypsum may be detected by treating a little of the pigment repeatedly with tepid water and testing the aqueous liquid for calcium and sulphuric acid.

Copper is tested for by digesting the minium with ammonia solution and filtering; in presence of copper the filtrate is bluish and after acidification with acetic acid gives the brown coloration with potassium ferrocyanide.

Lastly, artificial organic dyes are tested for by heating with alcohol (in presence of acid or alkali). If such colours are present, they may be identified, after fixation on wool, by the reactions given later, in the chapter dealing with textile fibres.

2. Moisture.—5 grams of the substance are heated at 100–110° to constant weight.

3. Insoluble Substances.—1 gram of the minium is heated on a water-bath with 15–20 c.c. of nitric acid diluted to twice its volume, a little sugar or hydrogen peroxide solution being added until the lead dioxide is dissolved. The liquid is then diluted with water and filtered through a tared filter, on which the insoluble part is washed with water until the wash water no longer gives the reaction for lead with hydrogen sulphide. The filter is ultimately dried at 105–110° and weighed.

4. Total Lead.—This is determined in the filtrate from the preceding determination or in an aliquot part of it by evaporating with sulphuric acid and then proceeding as in the determination of the soluble lead in white lead (*q.v.*, paragraph 6).

5. Lead Dioxide and True Minium.—The lead dioxide may be determined gravimetrically or volumetrically and the true minium (Pb_3O_4) then calculated.

(*a*) GRAVIMETRIC METHOD. 1 gram of the minium is heated on the water-bath for a quarter of an hour with 30 c.c. of dilute nitric acid (1 vol. diluted to 3). The liquid is diluted with hot water and allowed to settle, the clear liquid being decanted on to a tared filter and the insoluble part washed first by decantation and then on the filter until the wash waters no longer contain lead; it is then dried at 105–110° and weighed. This

represents lead dioxide plus insoluble matter ; deduction of the latter (determined as in paragraph 3) gives the lead dioxide.

(b) VOLUMETRIC METHOD. 1 gram of the minium is treated with 2·4 grams of potassium iodide and 30 grams of crystallised sodium acetate dissolved in a little water, 5 c.c. of glacial acetic acid being then added and the liquid shaken until the lead dioxide is completely dissolved. The solution is diluted to about 100 c.c. and the separated iodine determined by means of standard sodium thiosulphate solution in presence of starch paste : $I \times 0·94193 = PbO_2$.

CALCULATION OF THE TRUE MINIUM. $PbO_2 \times 2·866 =$ true minium.

$$*^*_*$$

Good minium should not be adulterated with extraneous substances or " improved " with organic dyes. Good commercial qualities usually contain 1–6% of insoluble matter and the best sometimes less than 1% ; in any case not more than 10% of insoluble residue should be allowed.

Absolutely pure minium of normal composition (Pb_3O_4) should contain 34·89% of PbO_2 ; the commercial products, however, usually contain an excess of the lower oxide and the percentage of dioxide varies commonly from 20 to 32, corresponding with about 57–92% of true minium.

CINNABAR, VERMILION

Cinnabar is mercuric sulphide obtained by sublimation and *vermilion* the same sulphide obtained in the wet way ; the former is more or less deep red and the latter bright red (scarlet).

Cinnabar and vermilion usually contain only small proportions of impurities from the prime materials ; vermilion may also contain impurities due to the method of preparation, namely, small quantities of metallic mercury, mercuric nitrate and free sulphur. These products are, however, often adulterated with ferric oxide, minium, chrome red, brickdust, gypsum, heavy spar, clay, ammonium chloride, dragon's blood, carmine and artificial organic dyes. Sometimes also arsenic and antimony sulphides are added to modify the colour.

The technical tests required for cinnabar and vermilion are more particularly those of the quality and intensity of the colour, the covering power, fineness, stability towards light and behaviour towards other pigments (white lead, zinc white) ; these are carried out by the general methods already indicated. The chemical analysis comprises principally the tests and determinations here described.

1. Fixed Residue.—2 grams of the substance are calcined in a porcelain crucible, which is heated at first gently and afterwards gradually more and more intensely to bright redness, the residue being weighed. If this is in appreciable quantity, it is analysed qualitatively, especially for lead, iron, chromium, silicates and barium and calcium sulphates.

2. Ammonium Chloride.—The substance is lixiviated with water and the liquid tested for ammonia by heating with caustic potash.

3. Organic Dyes.—The substance is treated with alcohol, coloration of the latter indicating the presence of artificial organic dyes or dragon's

blood ; the latter may be detected also by the peculiar empyreumatic odour emitted when the substance is heated.

The presence of carmine is revealed by moistening a little of the substance with ammonia on a filter-paper, the latter being coloured red if carmine is present.

4. Arsenic and Antimony.—A little of the substance is heated with caustic soda and filtered, the filtrate being acidified with hydrochloric acid and a current of hydrogen sulphide passed through it : a yellow precipitate indicates arsenic.

Another portion of the substance is boiled with concentrated hydrochloric acid and the liquid diluted somewhat and filtered ; hydrogen sulphide is passed through the filtrate, an orange precipitate denoting antimony.

5. Free Mercury and Mercuric Nitrate.—In absence of lead compounds, free mercury or mercuric nitrate may be detected by shaking the vermilion with nitric acid diluted to twice its volume, filtering the solution and treating with hydrogen sulphide : in presence of mercury or mercuric nitrate, a black precipitate is obtained. If, however, lead compounds are present, the precipitate should be examined by the ordinary methods of qualitative analysis to ascertain if it contains mercuric sulphide.

In absence of lead compounds mercuric nitrate may also be detected by moistening the substance with ammonium sulphide, a brown stain being produced.

6. Free Sulphur.—This is detected by extracting with carbon disulphide and evaporating the solvent, or by treating the substance with alkali and testing the solution with sodium nitroprusside.

**

Cinnabar or *vermilion* should not contain more than minimal traces of extraneous substances and should not leave more than traces of fixed residue on calcination ; they should not be " improved " with organic dyes. Vermilion in particular should be as free as possible from free mercury and mercuric nitrate, which lower its stability.

CADMIUM YELLOW

This consists of cadmium sulphide and, according to the conditions of its formation, exhibits various colours from pale lemon yellow to deep yellow and orange.

It may contain, as impurities or as additions, other cadmium compounds, zinc compounds and free sulphur, and it may also be adulterated with chrome yellow, cinnabar, arsenic sulphide, heavy spar and gypsum.

The technical tests for this pigment are mainly those of the tone and intensity of the colour, covering power, fastness to light and behaviour towards other pigments. Chemical analysis includes certain qualitative tests and possibly the determination of the cadmium sulphide, the procedure being as follows.

1. Qualitative Examination.—A little of the substance is heated in a glass tube : the colour should change to deep red and become yellow

again on cooling; a brown colour indicates the presence of carbonate or other cadmium salts; if a metallic mirror forms immediately on the tube, cadmium oxalate is present.

Another portion of the substance is boiled with water and filtered, the filtrate being tested with silver nitrate and with barium nitrate to ascertain if soluble chlorides or sulphates are present.

A little of the substance is treated with hot dilute hydrochloric acid; any insoluble residue remaining may contain especially barium sulphate or free sulphur, and sometimes cinnabar, arsenic sulphide, etc. If the hydrochloric acid solution is coloured, chrome yellow may be present and is easily identified. The solution gives a yellow precipitate with hydrogen sulphide; if the filtrate is rendered turbid by addition of ammonia and ammonium sulphide, zinc is present.

A further portion of the substance is digested with acetic acid and filtered, the filtrate being tested by the ordinary methods for cadmium (presence of hydroxide, carbonate or other compound of cadmium) and zinc (presence of zinc oxide or carbonate).

Lastly, a little of the substance is digested with ammonia and filtered, the filtrate being acidified with hydrochloric acid: if this gives a white precipitate, zinc oxide is present, or if a yellow coloration, arsenic is present.

2. Determination of the Cadmium Sulphide.—0·5 gram of the substance is digested with dilute acetic acid and filtered, the insoluble residue being washed and treated with dilute hydrochloric acid. The hydrochloric acid solution, filtered and diluted further with water if necessary, is treated with a current of hydrogen sulphide; the precipitated cadmium sulphide is collected, washed and treated in a porcelain crucible with dilute sulphuric acid, the excess of acid being evaporated by heating until evolution of sulphuric acid fumes ceases; the residue is gently calcined and weighed: $CdSO_4 \times 0\cdot693 = CdS$.

Green and Blue Pigments

The mineral substances used as blue or green pigments are principally : *Ultramarine*, composed essentially of an aluminium and sodium silicate and sodium sulphide; *ferric ferrocyanide* (*Prussian blue*) and *ferrous ferricyanide* (*Turnbull's blue*); *basic copper carbonates* (*Mountain green and blue* or *green and blue verditers*), *copper hydroxide* (*Bremen green and blue*), and *copper arsenite*, either alone (*Scheele's green*) or associated with *copper acetate* (*Schweinfurt green*); *chromium oxide and hydroxide* (*chrome green, Guignet green*), *basic chromium phosphates* (*Arnaudon green*, etc.); *cobalt aluminate* (*cobalt blue*); *zinc oxide* combined with *cobalt oxide* or *cobalt zincate* (*cobalt* or *zinc green*); *terre verte*, the colour of which is due to the presence of *ferrous silicate*. Use is also made of *mixed greens*, made up of a blue and a yellow pigment, the chief of these (mixed chrome greens) consisting of Prussian blue mixed with chrome yellow (*green vermilion*) or with other chromates.

TABLE XLII

Systematic Scheme for the Recognition of Blue and Green Pigments

With dilute hydrochloric acid in the hot				
completely soluble	is decolorised with evolution of hydrogen sulphide; the filtrate gives a white precipitate with ammonia—the substance is insoluble in sodium hydroxide and is not altered by calcination			*Ultramarine*
	solution green, turning intense blue with excess of ammonia: greens and blues with a basis of copper	with sodium hydroxide the substance does not dissolve, but blackens in the hot; on calcination it blackens	with HCl the s u b s t a n c e evolves carbon dioxide . . .	*Mountain green and blue*
			with HCl the substance does not evolve carbon dioxide. .	*Bremen green and blue*
		with sodium hydroxide the substance becomes blue, and in the hot yellow and then red; when calcined, it gives an odour of garlic, a brown residue and a white sublimate: *cupro - arsenical greens*	with HCl in the hot, the substance emits an odour of acetic acid	*Schweinfurt green*
			with HCl in the hot, the substance emits no odour of acetic acid	*Scheele's green*
	a pink solution, not precipitated by ammonium chloride and ammonia; when re-acidified with acetic acid it gives a yellow precipitate with potassium nitrite—the substance does not change when heated			*Cobalt green*
partially soluble	yellow solution, giving a blue precipitate with potassium ferrocyanide—the substance is insoluble in sodium hydroxide and becomes reddish brown when calcined			*Terre verte*
	greenish-yellow solution, blue residue; the solution gives the reaction for chromium with nitre and soda; the residue gives the Prussian blue reaction			*Mixed chrome greens*
almost insoluble	in concentrated acid it dissolves slowly and with difficulty, giving a green solution—the substance is insoluble in sodium hydroxide, becomes darker when calcined and gives a yellow mass when fused with nitre and soda			*Chrome green*
	in concentrated acid it dissolves, giving a green and then a yellow solution; on dilution a blue precipitate appears—by hot nitric acid the substance is decolorised; by sodium hydroxide it is decomposed, giving a reddish-brown residue and a colourless solution; on acidification a blue precipitate is formed—when calcined the substance decomposes, giving a brown residue .			*Prussian blue*
insoluble—also insoluble in nitric acid or sodium hydroxide; it is not altered by calcination				*Cobalt blue*

Less commonly use is made as pigments of other copper compounds such as the stannate (Gentele's green), oxychloride (Brunswick green), basic sulphate (Casselmann's green) and basic acetate (verdigris) ; silicate of cobalt and potassium (Smalt), cobalt stannate (cœruleum), cobalt phosphate and arsenate (cobalt violet) ; barium manganate (manganese green) and manganese phosphate (manganese violet).

The scheme on p. 389 indicates reactions for the ready distinction of the principal blue and green pigments (when these are not complex mixtures). Below are described the methods of complete analysis of some of the more important of these.

ULTRAMARINE

This is a complex compound of aluminium and sodium silicate and sodium sulphide. The typical and most common ultramarine is *blue ultramarine*, which forms a very fine powder (microscopically crystalline) of a pure blue, reddish blue or greenish blue colour according to the proportions of the components and the method of preparation ; ultramarines of other tints, especially *green* and *violet ultramarines*, are also made. Ultramarine may be adulterated with gypsum, chalk, clay, heavy spar, zinc white and magnesium carbonate and may also be mixed with glycerine and glucose.

It is subjected mainly to certain technical (*see* 1–5) and qualitative tests (*see* 6 and 7) ; quantitative analysis (*see* 8) is rarely required.

1. Quality and Intensity of the Colour.—The colour is compared with that of a standard ultramarine by pressing a pinch of each on a piece of white paper with a spatula.

To measure the intensity of the colour, a scale of comparison is prepared by making intimate mixtures of 1 gram of the standard ultramarine with different amounts of an indifferent white substance (kaolin), e.g., with 10 grams for the normal intensity, and with 9, 8, 7, 6 . . . or 11, 12, 13, 14 . . . grams for greater and less intensities. A mixture of 1 gram of the ultramarine to be examined with 10 grams of the same white substance is made and compared with the scale of mixtures.

2. Fineness.—The ultramarine is sieved through the finest silk sieve to see if any particles are retained ; if so, these are tested to ascertain if they can be easily crushed with the fingers so as to pass through the sieve.

Further 1 gram of the ultramarine is shaken with 200 c.c. of water in a glass cylinder and then left at rest : the longer the time taken to settle— for the bluish tint of the water to disappear—the finer the sample.

3. Oil Colour Test.—1 gram is mixed on a glass plate with a few drops of good, boiled linseed oil and then spread out on the glass and allowed to dry ; the colour is compared with that given by a standard ultramarine.

4. Printing Tests.—In printing or stamping, ultramarine is used mostly with albumin. Some qualities of ultramarine cause putrefaction of the albumin and are hence little suitable for this purpose. To test the behaviour towards albumin, 2 grams of the ultramarine are well mixed with 2 grams of albumin and 10 c.c. of hot water and then left at 25–30°

for 24 hours ; the less marked the unpleasant odour and the less changed the appearance of the mixture, the better is the ultramarine.

5. Resistance to Alum.—0·1 gram of the ultramarine is shaken with 10 c.c. of 10% alum solution, the value of the ultramarine increasing with the length of time it retains its colour under these conditions.

6. Free Sulphur.—About a gram of the substance is carefully heated in a test-tube ; if no appreciable amount of free sulphur is present, no deposit, or scarcely any, of sulphur will form on the cold parts of the tube.

7. Extraneous Substances.—From 1 to 2 grams of the ultramarine are boiled with hydrochloric acid and filtered. If the ultramarine is pure, the insoluble residue is composed exclusively of silica with small quantities of alumina and a little sulphur ; if the sample contains barium sulphate or alumina in considerable quantity, it is adulterated with heavy spar or clay.

The solution should contain only alumina or soda if the ultramarine is pure ; it may contain zinc, calcium or magnesium if it is adulterated with zinc white, gypsum, chalk, or magnesium carbonate.

Glycerine may be detected by the odour of acrolein emitted on calcining the ultramarine, and glucose by lixiviating with water and testing the solution with Fehling's solution.

8. Quantitative Analysis.—This includes mainly determinations of the thiosulphates, sulphates, chlorides, total sulphur, silica, alumina and soda.

(*a*) THIOSULPHATES, SULPHATES, CHLORIDES. In a 500 c.c measuring flask 10 grams of the substance are shaken with water, the liquid being then made up to volume, left to stand for some time and filtered.

In 100 c.c. of the filtrate the *thiosulphates* are determined volumetrically by means of standard iodine solution and are calculated as *sodium thiosulphate* in 100 parts of the substance (*see also* Vol. I, p. 108).

In another 100 c.c., acidified with hydrochloric acid, the *sulphates* are precipitated with barium chloride and weighed as usual, the result being calculated as *sodium sulphate* per 100 parts of the substance.

In another 100 c.c. the *chlorides* are determined volumetrically and calculated as *sodium chloride*.

(*b*) SILICA AND TOTAL SULPHUR. 1 gram of the substance is well mixed with a little water in a porcelain dish, 1–2 c.c. of bromine being gradually added and after some time 15–20 c.c. of concentrated nitric acid. The liquid is evaporated to dryness, taken up with hydrochloric acid and water and again evaporated to dryness : the residue is finally digested for some hours with a little concentrated hydrochloric acid, then diluted with boiling water and filtered, the insoluble residue being well washed with hot water. The calcined and weighed residue represents the silica (also any undecomposed silicates and barium sulphate, if present).

In the filtrate the sulphuric acid is precipitated with barium chloride in the ordinary way : $BaSO_4 \times 0·13738 =$ total sulphur.

(*c*) ALUMINA AND SODA. 1 gram of the substance is treated with water and hydrochloric acid, first in the cold and afterwards in the hot, the liquid being then evaporated to dryness, and the residue taken up in hydrochloric

acid and hot water and filtered, and the insoluble residue washed.   In the filtrate and washings, the alumina is precipitated by slight excess of ammonia in the hot and the precipitate weighed as usual.

The filtrate from the alumina is acidified with sulphuric acid and a little nitric acid and evaporated to dryness, the residue being calcined and weighed : $Na_2SO_4 \times 0.4364 = Na_2O$.

**

Good ultramarine should be in very fine powder and of a pure and intense colour ; it should be free from extraneous substances and should contain only traces of soluble salts and free sulphur.   Its composition varies within fairly wide limits, commonly as follows :

Silica (SiO_2)	29–47%
Alumina (Al_2O_3)	22–35%
Soda (Na_2O)	15–28%
Sulphur	5–14%

The mean composition is approximately : SiO_2, 38 ; Al_2O_3, 26 ; Na_2O, 24 ; and S, 12%.

Free sulphur may sometimes amount to 1% or more.

PRUSSIAN BLUE, TURNBULL'S BLUE

The former of these is a ferric ferrocyanide, and the latter a ferrous ferricyanide.   Both are in powder or masses of deep turquoise blue with reddish reflection ; the lighter and more spongy forms are the more highly valued.

They may contain as impurities, small quantities of alkali, sulphates and chlorides and are often adulterated with kaolin, heavy spar, gypsum, chalk, white lead, zinc white, magnesia, starch, etc.

The purest and best qualities of Prussian blue are also sold as *Paris blue* ; the *Prussian blue* of commerce usually contains some of the above substances to give it a lighter colour.

Besides the technical tests, among which particular interest attaches to the intensity of the colour, fastness to light, behaviour when mixed with zinc oxide, yellow pigments, etc., and with vehicles (oils), it may be necessary to test qualitatively for impurities and to determine quantitatively the colouring matter, the methods employed being described below.

1. Impurities.—2 or 3 grams of the substance are treated with hot caustic soda solution, the liquid being diluted and filtered and the insoluble part washed and then dissolved in hot dilute sulphuric acid ; any undissolved residue may contain especially silica or silicates and barium sulphate, these being identified by the ordinary methods.   The alkaline solution is tested for sulphates and chlorides.

On the other hand about 2 grams of the substance are gently calcined with 2 grams of ammonium nitrate and 6 grams of ammonium sulphate. The residue is treated with hot dilute hydrochloric acid, the silica, silicates, barium sulphate and part of the gypsum remaining undissolved ; the solution is tested for alumina, zinc, lime, magnesia and alkalies by the usual methods.

Starch may be detected by heating the substance with water, filtering, and testing the cooled liquid with tincture of iodine.

2. Determination of the Colouring Matter.—4 grams of the blue are thoroughly mixed with water, introduced into a 200 c.c. measuring flask, rendered alkaline with soda, boiled for a few moments, cooled, made up to volume, shaken and filtered. 50 c.c. of the filtrate (= 1 gram of substance) are acidified with sulphuric acid and titrated with potassium permanganate solution (1·20 gram per litre). If n c.c. of permanganate are used, the percentage of the colouring matter will be

$$\frac{100 \times n}{51 \cdot 6}$$

in the case of Prussian blue, or

$$\frac{100 \times n}{48 \cdot 8}$$

in that of Turnbull's blue.

GREENS AND BLUES WITH A COPPER BASIS

Two groups may be distinguished, according as arsenic is present or absent.

One of the most important cupro-arsenical greens is *Schweinfurt green*, which is a double salt of the normal acetate and arsenite of copper of the formula, $Cu(C_2H_3O_2)_2, 3CuAs_2O_4$. It is a green, microcrystalline powder, its colour deepening with the size of the crystals. It is often mixed with other substances, such as gypsum, chalk, kaolin, heavy spar, lead sulphate, chrome yellow, zinc yellow, etc., either fraudulently or to modify the colour ; some of these mixtures are sold under various names. Another green, analogous to the above, but far less used, is *Scheele's green*, which is a more or less basic copper arsenite,

Of the arsenic-free pigments the best known are *Mountain green and blue* (basic copper carbonates) and *Bremen green and blue* (copper hydroxides) ; use is made, but less commonly, of greens based on the basic acetate, basic sulphate, oxychloride and stannate of copper, already mentioned. All these products may be adulterated with the usual extraneous white substances, such mixtures being given special names.

Examination of these products comprises firstly the technical tests relating to intensity, fastness and behaviour in mixtures, and further, qualitative analysis for the determination of the nature of the product and of any adulterations, and also certain quantitative determinations. The qualitative investigation is carried out as in paragraph 1 and the quantitative determinations as in paragraphs 2 and 3

1. Qualitative Examination.—A little of the substance is heated to redness in a test-tube : emission of a garlic-like odour and formation of a white sublimate indicate arsenic, whereas if the substance blackens without giving such odour or sublimate, arsenic is absent.

A little of the substance is heated with sodium hydroxide solution : if

it blackens without dissolving, the pigment is non-arsenical, but if it becomes yellow and then red, arsenic is present.

A little of the substance is heated with dilute hydrochloric or sulphuric acid : if an odour of acetic acid is emitted, copper acetate is present.

The substance is treated with excess of ammonia in the cold : pigments with a copper basis mostly dissolve giving an intensely blue coloration ; any insoluble residue represents extraneous substances, which are recognised by the ordinary reactions.

The pigment is treated with hydrochloric acid : effervescence indicates copper or calcium carbonate ; any insoluble residue may contain barium sulphate, gypsum (in large quantity), lead sulphate or clay, which may be identified by the usual methods. The solution is treated with excess of ammonium carbonate : if a precipitate forms, it is tested especially for alumina, lime and magnesia.

In investigating yellows with a chromium basis, the pigment is dissolved in concentrated hydrochloric acid and the solution diluted with water and treated with sulphuric acid : a white precipitate indicates presence of lead. The liquid is heated to boiling with a little alcohol and then treated with excess of ammonium carbonate, which precipitates the chromium as the green hydroxide.

2. Determination of the Copper.—1 gram of the substance is dissolved in hydrochloric acid and the solution treated with excess of ammonium carbonate and filtered, the insoluble portion being well washed ; the filtrate is boiled and the copper precipitated by means of sodium hydroxide, the precipitate being filtered off, washed, calcined and weighed as copper oxide.

3. Determination of the Arsenic.—This is carried out with Schweinfurt green, which may contain it, besides as copper arsenite, also partly as free arsenious anhydride, this being recognisable under the microscope by its octahedral form.

For the determination, about 0·3 gram of the finely-powdered substance is treated in a beaker with 25 c.c. of water, concentrated hydrochloric acid being then added drop by drop until the pigment is dissolved ; as a rule not more than 10 drops are required.   If free arsenious anhydride is present in appreciable amount, it remains undissolved under these conditions and may be filtered off and washed.   The filtrate is treated with sodium carbonate to incipient precipitation and then with a solution of 2–3 grams of sodium potassium tartrate ; it is next diluted to about 200 c.c., mixed with about 5 grams of solid sodium bicarbonate and titrated with iodine solution in presence of starch paste ; in this way the combined arsenious anhydride is determined.

The free arsenious anhydride remaining on the filter is washed with water into a beaker and dissolved by boiling with sodium bicarbonate, the liquid being then titrated with iodine.

**

Schweinfurt green of normal composition should contain 31·4% of CuO and 58·5% of As_2O_3 ; commercial pure products usually contain 27–31% of CuO and 50–58% of combined As_2O_3.   Free arsenious anhydride should not exceed 1–2%, but in certain qualities it may be as much as or even more than 5%.

CHROME GREEN

Chrome green proper consists of chromium sesqui-oxide, *Guignet green* being more or less hydrated oxide. Other analogous products, such as *Arnaudon's*, *Plessy's* and *Schnitzer's greens*, consist essentially of basic chromium phosphates.

These pigments may be adulterated with various inert substances, and in some cases the colour is heightened or modified by addition of other pigments or of artificial organic dyes.

The tests to be made on such products consist mainly in the technical tests of the quality and intensity of the colour, covering power, fastness to light and to atmospheric and chemical agents and behaviour towards other pigments ; these tests are made by the ordinary general methods. As regards chemical analysis, this is usually limited to a qualitative examination for the detection of any adulterations.

Qualitative Investigation.—A little of the substance is treated with hot dilute hydrochloric acid ; the chrome green does not dissolve, whereas several of the extraneous substances which it may contain pass into solution at any rate partially, e.g., calcium and magnesium compounds, yellows with a chromium or iron basis, and greens with a copper basis ; these substances may be detected in the solution by the ordinary methods.

Another part of the substance is melted in a platinum crucible with nitre and sodium carbonate, the mass obtained being dissolved in water ; any insoluble residue may contain especially ferric oxide. The solution is acidified with hydrochloric acid, boiled for a long time with alcohol and evaporated almost to dryness, the residue being taken up in water and filtered from any silica which separates ; the filtrate is tested for the metals, phosphoric acid and boric acid (derivable as an impurity from the manufacturing processes) by the ordinary qualitative methods.

For the detection of artificial organic dyes, *see* General Methods.

MIXED CHROME GREENS

These are mixtures of a yellow with a chromium basis with a blue, usually Prussian blue, and are often improperly termed *chrome greens*. The commoner ones consist of chrome yellow and Prussian blue, often mixed with various other substances ; such are *green, vermilion* and the like. Use is sometimes made also of mixtures of zinc yellow and Prussian blue (in some cases improperly termed *zinc greens*).

These pigments almost always contain a considerable proportion of extraneous substances, either white (gypsum, kaolin, barium sulphate, etc.), or coloured (ochres, blacks), and in some instances they contain copper pigments or ultramarine.

The investigation of these pigments includes, besides technical tests, also tests for the detection of extraneous substances, these being carried out by the ordinary methods (*see* Chrome yellow and Prussian blue). Sometimes the lead chromate and Prussian blue are determined, the following methods giving sufficiently exact results.

1. Lead Chromate.—This is determined exactly as described for lead chromate in chrome yellows (*q.v.*, paragraph 2).

2. Prussian Blue.—4 grams of the pigment are thoroughly mixed in a mortar with 10 c.c. of water and 5 c.c. of hydrochloric acid. After addition of 20 c.c. of 20% ferrous sulphate solution the liquid is left to digest for 10 minutes, excess of caustic soda being then added and the whole transferred to a 200 c.c. flask—the mortar being washed out with the least possible quantity of water. The liquid is heated almost to boiling, allowed to cool, made up to the mark, mixed and left to clear, 100 c.c. of the clear liquid being acidified with sulphuric acid and titrated with 0·12% potassium permanganate solution. If n is the number of c.c. of the latter used, the percentage of Prussian blue in the pigment is given by the formula :

$$\frac{n \times 12 \cdot 5}{12 \cdot 9}.$$

***

Mixed chrome greens usually contain considerable quantities (up to 80–90%) of inert substances ; in the commoner types the content of lead chromate varies from 3 to 10% and that of Prussian blue from 5 to 20%.

TERRE VERTE

Terre verte or *Veronese earth* is a magnesium clay coloured by ferrous silicate. It is very rich in silica and poor in alumina and usually contains, besides magnesia, also small quantities of alkali, and sometimes lime and carbonic acid.

It is often " improved " with organic dyes (generally malachite green or one of its allies) and sometimes with copper green. It may, indeed, be replaced by inert matter coloured with artificial organic dyes.

The examination of terre verte is commonly limited to technical tests of the covering power and of the fastness to atmospheric agents and to lime, and to tests for the presence of artificial organic dyes (usually by treatment with alcohol). The presence of copper colours may be detected by treatment with ammonia.

Brown, Grey and Black Pigments

The most common of these pigments are : certain earths, such as *Sienna* or *Italian earth*—which is a *brown ochre—umber, Cologne earth* or *Cassel brown ; blacks with a carbon basis ; graphite*, consisting of more or less impure crystalline carbon.

More rarely use is made for this purpose of other substances, such as slate grey, which is ground natural slate, blackish to grey in colour ; certain pulverised lignite pitches ; lignite and peat blacks, obtained by the carbonisation of these substances ; Prussian black and brown, consisting respectively of carbon and metallic iron and of carbon and oxide of iron. Mention may also be made of copper chromite (Persoz black), anhydrous

manganese peroxide (manganese black) and hydrate (manganese brown), lead peroxide, copper ferrocyanide (Florentine brown) and zinc greys, which may consist of powdered zinc minerals or of so-called zinc dust or zinc oxide mixed with carbon.

The reactions indicated in the scheme of Table XLIII serve for the differentiation of the more important black and brown pigments, which are considered separately in the following paragraphs. For the examination of Italian or Sienna earth, which in the natural state may exhibit various

TABLE XLIII

Systematic Scheme for the Recognition of Brown and Black Pigments

When heated to redness in the air, the substance

burns

- emits no bituminous odour; the substance remains black when treated with hydrochloric acid or with sodium hydroxide
  - burns without leaving ash . *Lamp black*
  - leaves a little alkaline, whitish or greyish ash, largely soluble in hydrochloric acid . . . . . *Vegetable blacks*
  - leaves much grey or reddish ash, almost insoluble in hydrochloric acid . . . *Slate black*
  - leaves a very large amount of white ash soluble in hydrochloric acid . . . *Animal black*
- emits bituminous odour and leaves only little slightly coloured ash—the substance is almost insoluble in hydrochloric acid and partially soluble in sodium hydroxide, giving a dark brown liquid . . . . *Cologne earth*

does not burn

- evolves water and becomes reddish-brown—when fused with nitre and sodium carbonate the substance gives a dark green mass—the substance is partially soluble in hydrochloric acid, giving a yellow solution, which yields a blue precipitate with potassium ferrocyanide . . . . *Umber*
- changes from yellowish-brown to reddish—when fused with nitre and sodium carbonate it gives a more or less deep green mass—the substance behaves like the preceding with hydrochloric acid and is insoluble in sodium hydroxide. . . . *Italian or Sienna earth*
- remains reddish-brown or varies but little; when fused with nitre and sodium carbonate it gives a green mass; with hydrochloric acid or sodium hydroxide like the preceding . . . . *Burnt Sienna and umber*
- remains blackish or unaltered; the colour is not altered by hydrochloric acid or sodium hydroxide . . . . *Graphite*

gradations of colour from yellow to brownish yellow or to dark brown, *see* Ochre (above).

UMBER

This is a variety of ochre containing large proportions of hydrated ferric oxide and oxides of manganese and also small quantities of humous substances.

In the *natural* state it occurs as more or less dark chestnut-brown lumps or powder, rich in moisture. It is also lixiviated and *dried* before sale and then contains far less water. *Burnt* umber is also used, this being reddish-brown or light brown and freed from humous matter and from most of the water.

Its examination is usually confined to the technical tests relating to fineness, covering power, etc., and to a few chemical investigations, such as those described in paragraphs 1-4, which serve mainly to distinguish natural from burnt umber. If complete analysis is required, this may be carried out by the methods already given for clays (Vol. I, p. 144).

1. Hygroscopic Water.—5 grams of the substance are dried in a platinum dish in an oven at 100–105° to constant weight, the loss representing hygroscopic water.

2. Loss on Calcination.—The residue from the preceding determination is heated to redness in a muffle, the loss of weight thus caused representing combined water, organic matter and the carbon dioxide of any little calcium carbonate present.

3. Behaviour towards Potash.—A small quantity of the substance is boiled with about 20% caustic potash solution : if the liquid becomes more or less brownish-yellow, humous substances are present (natural or dried umber) ; if the liquid remains colourless, these are not present (burnt umber).

4. Behaviour with Lead Peroxide.—A little of the substance is boiled for a few moments with nitric acid and lead peroxide; after standing, the liquid appears red owing to the presence of manganese ; with the natural earth the coloration is, however, slight, whilst with the burnt earth it is much more intense. It is well to make this test in comparison with typical products.

* * *

Natural umbers contain somewhat variable amounts of *hygroscopic water* (up to 20% or more), and the *loss on ignition* usually varies from 7 to 11%. The *dried* earth contains much less hygroscopic moisture (about 6%), but the whole of the combined water, so that the loss on calcination is the same as with the natural earths. The *burnt* earth contains little hygroscopic water (usually less than 5%) and give a loss of 3-4% on calcination. In general it may be said that when an umber loses less than 5% on calcination, it is burnt —this independently of the hygroscopic water, which may be considerable even in burnt umber if this has been stored in a moist place.

In addition to water, natural umber may contain up to 10% of *organic matter* ; as regards the mineral components, these may vary within fairly wide limits, which are approximately as follows ; silica, 4-30% ; alumina, 3-13% ;

ferric oxide, 22–52% ; oxides of manganese, 7–20%. Small quantities of calcium carbonate and sometimes of calcium sulphate may also be present.
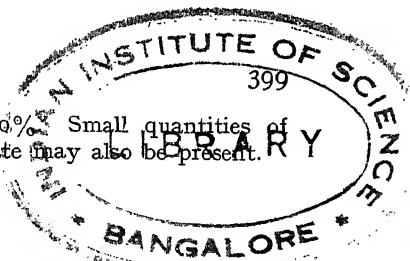
COLOGNE EARTH

This is a species of earthy peat, ground and suitably purified. It consists principally of humous and carbonaceous matter. It forms a light, brown powder, which, when heated in the air, burns with moderate ease, giving no flame and emitting a bituminous odour. It may be mixed with ochre, umber and ferric oxide, such mixtures (*prepared Cologne earth*) being sold under various names.

Its examination includes, besides the usual technical tests, the following chemical tests, which indicate mainly if the Cologne earth is pure or mixed with any of the substances indicated above.

1. Ash.—5 grams of the substance are carefully burnt in a platinum dish and then calcined in a muffle, the residue being weighed and its colour noted.

2. Hydrochloric Acid Test.—A small quantity of the substance is boiled with hydrochloric acid and filtered ; if the filtrate is yellow, it is tested for oxide of iron.

3. Potash Test.—A small quantity of the substance is boiled with 20% caustic potash solution, in which it should largely dissolve, giving a dark brown liquid which, when neutralised with hydrochloric acid, yields a flocculent, brown precipitate.

* * *

Cologne earth, if pure, does not leave more than 10% of ash, which is whitish or faint pink, and does not contain more than traces of iron ; if the ash exceeds this amount and is red, the product is mixed with umber, ochre or ferric oxide.

Further, pure Cologne earth gives up not more than a trace of iron to hydrochloric acid, and when treated with caustic potash it should not leave an abundant heavy residue.

GRAPHITE

This consists of more or less impure carbon mixed with ferruginous sand or with clay and other silicates. It is lead grey or blackish, shining, and greasy to the touch.

Its value depends principally on the carbon content. This cannot be determined by direct combustion unless the graphite is burnt in a current of oxygen, since in the air it burns with extreme difficulty. More usually, and with sufficient exactitude, the carbon is determined by mixing about 0.5 gram of the graphite intimately with 20–30 grams of litharge, placing the mixture in a refractory earthenware crucible, covering with a little litharge and heating the covered crucible in a furnace to complete fusion ; when cool the regulus of lead obtained is extracted, cleaned and weighed : 34.5 parts of lead correspond with 1 part of pure carbon.

* * *

The *purer graphites* contain up to 95% or more of *carbon*, the more usual qualities containing 60–80% and the impure ones less than 50%.

BLACK PIGMENTS WITH A BASIS OF CARBON

The principal of these are : *Soot black,* which includes *resin black, tar black, lamp black* and *acetylene black* ; *slate black,* obtained from bituminous shales ; *lignite black* and *peat black* ; *vegetable blacks,* including *charcoal black, vine black, pine black,* etc. ; *animal blacks,* the chief of these being *bone black* and others *ivory black, horn black,* etc.

Mixtures of these blacks either with one another or with inert materials are also sold, sometimes under special names.

The examination of black pigments comprises certain technical and physical tests, indicated in paragraphs 1–3, and also chemical tests and determinations (paragraphs 4–7) for the purpose either of distinguishing the different products from one another (especially the determination and examination of the ash) or of ascertaining their purity and value.

1. Quality and Intensity of the Colour.—These are determined by the general methods, particular care being taken to note if the colour is a pure black or if it shows more or less traces of brown, reddish, greenish, etc. ; as regards the intensity, it is well to examine black pigments—always in comparison with a typical black—with reference to their behaviour when mixed not only with a white but also with other pale pigments.

2. Covering Power.—This is determined by mixing 5 grams of the pigment with 10 grams of spirit and 100 c.c. of 10 % gum solution. A dry brush is dipped into the mixture and then weighed, a sheet of white writing paper, divided into square centimetres, being painted with it and the brush again weighed ; the weight of pigment used for a certain number of sq. cm. is thus determined. A similar procedure is followed with a standard black and the colours compared.

3. Specific Gravity.—This is determined more especially with soot black by means of a picnometer at 15° C., alcohol of at least 95 % concentration being employed as liquid.

4. Detection and Determination of Empyreumatic Substances.—Soot black and other blacks, if not well calcined, may contain empyreumatic or tarry substances, which alter the tone of the colour.

To recognise their presence, a little of the pigment is moistened with alcohol or benzene on a sheet of white paper, mixed somewhat with the tip of the finger and allowed to dry ; the black powder is then removed and the other side of the paper examined to see if any spot remains ; in presence of empyreumatic substances a yellow or brown spot is left.

These substances may be determined (1) by lixiviating 2–5 grams of the pigment with benzene until the solvent is no longer coloured and then weighing the residue, or (2) better, as volatile substances (*see* below).

5. Volatile Matter.—This includes moisture and empyreumatic or tarry substances. The moisture may be determined separately by drying the pigment at 100°. The total volatile substances are determined by weighing 2–5 grams of the pigment in a porcelain crucible furnished with a perforated cover, compressing it and then calcining in a slow current of hydrogen until the flame of the latter ceases to be luminous ; loss in weight represents volatile matter.

6. Determination and Examination of the Ash.—5 grams of the pigment are calcined in a flat porcelain dish in a muffle at a red heat until all the particles of carbon have disappeared, the residue being weighed.

The colour of the ash, its solubility in hydrochloric acid, and its neutrality or alkalinity are noted ; a qualitative analysis may be made, with reference especially to the silica, alumina, ferric oxide, lime, magnesia, alkalies, phosphates, carbonates, sulphates and chlorides.

Only rarely are certain quantitative determinations necessary on the ash, such as those of the silica and alumina in mineral blacks, lime, alkalies and phosphates in vegetable blacks and calcium phosphate in animal blacks.

7. Other Tests.—In some cases a small quantity of Prussian blue is added to black pigments and especially to soot black to correct any tendency to reddish brown. This may be detected by boiling the pigment with alkali and filtering, and treating the filtrate, after acidification, with ferric chloride, which gives a blue precipitate.

Bone black which has been recently prepared and not washed contains small quantities of calcium cyanide, which may be detected by extracting about 200 grams of the pigment with cold water and evaporating the filtrate to very small volume with a few drops of ammonium sulphide ; this procedure yields calcium thiocyanate, which is recognisable by its reaction with ferric chloride.

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The nature of a black pigment and its adulterations may be ascertained more particularly from the quantity and quality of the ash.

In general *soot black* leaves only traces of ash. It often contains empyreumatic substances, which are usually in small amount, but in some cases, with products not well burnt, may reach 10–15% or more. The different types of soot black may be differentiated by the specific gravity : for resin black this does not usually exceed 1·70, whilst for lamp black and acetylene black it is always greater than this and is sometimes 2 or more.

Slate black always leaves 50% and sometimes 60% or more of ash, which is dark grey, sometimes with a reddish tint ; it is almost insoluble in hydrochloric acid and consists of aluminium silicate with a greater or less proportion of iron.

Lignite black leaves little yellowish ash, only partially soluble in hydrochloric acid and consisting of aluminium silicate with a considerable amount of iron and calcium sulphate ; the ash of peat black is similar, but usually contains also small quantities of phosphoric acid.

Vegetable black gives little ash (usually not more than 4–5%), which is pale grey and alkaline and largely soluble in hydrochloric acid ; its principal constituents are lime, magnesia, potash and phosphoric acid.

Lastly, *bone black* leaves about 80% or more of white ash, almost completely soluble in hydrochloric acid and consisting largely of calcium phosphate, with small proportions of calcium carbonate and traces of silica, gypsum, ferric oxide, magnesia and alkalies.

Metallic Pigments

These colours, termed also *bronze pigments*, generally consist of finely powdered metals or metallic alloys, sometimes partially oxidised or sulphided to obtain definite colours. The principal metals used for this pur-

pose, besides silver and gold, are : copper, its alloys with zinc and tin (brasses, bronzes, etc.), argentan, tin and its alloys with lead and antimony, aluminium and sometimes antimony.

Metallic pigments are sometimes mixed with adhesives or fatty substances and may be " improved " with artificial organic dyes.

Besides powdered metals, certain metallic compounds are sometimes used for the same purposes, e.g., stannic sulphide (mosaic gold), antimony sulphide (iron bronze) and various oxygenated compounds of tungsten (tungsten bronzes).

The examination of metallic pigments is usually restricted to a few technical tests (covering power, printing tests) and to qualitative tests (for gum, fatty substances, artificial organic dyes, metals), the ordinary methods being employed. In rare cases determinations are required of the separate metals, the methods already described in the chapter on metals (Vol. I) being then used.

Lakes

These are pigments formed from an organic colouring matter fixed on a substance (*base*) which is usually inorganic.

The colouring matter may be an artificial organic dye or a vegetable colour (extracts of dye wood or of other parts of plants, indigo) or an animal colour (cochineal) ; lakes are also made with mixtures of several colouring matters.

In the commoner cases the base is a hydrated metallic oxide (of aluminium, tin, lead, zinc or, less often, chromium, iron, copper, antimony) to which the colouring matter (if acid) is united by true chemical combination ; tannin lakes are also made (with basic colouring matters). In other lakes the base is an inert substance (barium sulphate, precipitated alumina and silica, chalk, gypsum, kaolin, etc.), on which the colouring matter is fixed by simple mechanical absorption. Lakes of the former kind may be mixed, either fraudulently or for the purpose of attenuating the colour, with inert materials.

Examination of lakes includes technical tests directed to the determination of their fitness for the proposed purpose, and also a chemical analysis, usually only qualitative, to ascertain the nature of the colouring matter and of the base from which the lake is formed.

1. Technical Tests.—These vary with the use to which the lake is to be put.

In all cases importance attaches to tests of the *tone* and *intensity* of the colour and of the *fastness to light,* these being carried out in the ways indicated for other pigments (*see* General Methods).

With lakes for lithographic and printing colours and those for the use of artists, the *covering power* (or, in some cases, the *transparency*) is of interest ; it is measured by the methods already described, especially by noting if black lines on a white paper are visible through the colour suitably mixed and spread in a uniform layer and dried.

With lakes for lithographic and printing purposes and those for coloured paper and pictures, the *fastness to water* is of importance. In the first case a little of the pigment is mixed with a lithographic varnish and marks made with it on a white paper and allowed to dry; the paper is then either immersed in cold water or covered with a moist filter-paper and left for 1-2 hours: if the water or the filter-paper becomes coloured in this time, the lake is not resistant to water. In the second case, that is, with lakes for coloured paper and pictures, the test is made by spreading a little of the lake mixed with glue on thick paper and, after drying, pouring a few drops of water on the wrong side of the paper and leaving for about 15 minutes; the excess of moisture is then removed by means of filter-paper and the remainder allowed to dry, note being then made if the positions of the water drops are marked by coloured spots.

Lithographic and printing lakes should also be *resistant to spirit varnishes*, when the latter are used as a protection or to render the colours less brilliant. To test lakes from this point of view, it suffices to subject a sharply outlined print to the action of a few drops of spirit varnish, which covers partly the design and partly the white ground. After a few minutes the excess of the varnish is poured off and the print examined when dry to see if the ground has remained perfectly white and if the outlines of the design are still sharp.

In some cases the *resistance to moisture and heat* must be determined. For this purpose, strips of paper painted with the lake—suitably mixed—and dried are exposed to steam from boiling water for some minutes and again dried and examined to see if the colour has altered.

Lakes for coloured paper and pictures are also tested as to their *fastness to lime and to alkali*, this being done as described in the general methods or, more simply, by moistening with milk of lime or dilute (about $N/10$) caustic soda solution the reverse side of a paper painted with the lake and examining the right side of the paper after drying, to ascertain if any change of colour has occurred.

2. Examination of the Colouring Matter.—Identification of the colouring matters contained in lakes is not always easy, since lakes are often made with mixtures of colours and the properties of the latter may be modified in their precipitation in the form of lakes or in their separation from these.

As far as is possible, the colouring matters of lakes are investigated by extracting and isolating them by means of solvents and testing the solutions obtained, and partly also by testing the lake itself with suitable reagents.

Many lakes give up their colouring matter to alcohol; in such case the extraction is effected by heating the lake repeatedly with strong alcohol. The filtered alcoholic solution is carefully evaporated, best after dilution with twice its volume of alcohol: if the colouring matter is soluble in water it remains in the aqueous solution, but in the contrary case it is precipitated.

When the colouring matter is not dissolved in the alcohol, it may often be separated by means of dilute hydrochloric acid, care being taken to avoid excess—an amount insufficient to decompose the whole of the lake taken is used. The acid and lake are shaken for some time in the cold and then

diluted with water and filtered. Acetic acid is also sometimes used for the extraction of the colouring matter.

The colouring matter separated from the lake or its solution is tested in the manner indicated later for the identification of the various organic dyes, both natural and artificial.

In general, alcohol extracts more or less completely from their lakes the following colouring matters : azo- (e.g., Soudan dyes and their analogues), aminoazo-, sulphonated indulines, safranines, triphenylmethane derivatives and phthaleins (eosin and rhodamine, with fluorescence). No colouring matter, or but little, is given up to alcohol by the lakes of sulphonated azo-dyes, sulphonated triphenylmethane derivatives, mordant dyes such as those of the alizarin group and most of the natural organic colouring matters.

3. Investigation of the Base.—A few grams of the lake are heated in a porcelain crucible until the colouring matter is completely burnt away. Evolution of any gases or vapours of special odour during the heating is noted, a garlic-like odour indicating the presence of arsenic in the lake.

The residue of the calcination is treated with hydrochloric acid, the solution and any insoluble residue remaining being then analysed by the ordinary methods. Tests are made especially for alumina, zinc oxide, tin oxide, lead oxide, barium sulphate and calcium carbonate, and also for oxides of chromium, iron, copper and antimony, silicates and gypsum.

* *

The more common and more important *red lakes* are those of cochineal, red wood, alizarin (or madder) and its derivatives, triphenylmethane dyes (fuchsine), safranine, eosin, developed and sulphonated azo-dyes ; the last give also *orange lakes*.

Noteworthy among the *yellow lakes* are those of yellow wood, quercitron, Persian berries, naphthol yellow, auramine, thioflavine, chrysoidine, quinoline yellow, metanil yellow and its analogues.

Of the *blue lakes*, mention may be made of those of indigo and logwood, alizarin blue, basic triphenylmethane blues and methylene blue. *Violet lakes* are made with methyl violet and the like or with mixtures of blues and reds.

Green lakes have bases of chlorophyll, malachite green and other greens derived from triphenylmethane, or are mixtures of blue and yellow lakes.

Brown and *black lakes* are made with logwood and iron salts, with cutch or with Bismarck brown.

Lakes of natural colours and those of alizarin are among the most stable and valuable. Eosin lakes and those of basic triphenylmethane dyes are very brilliant in appearance, but readily undergo alteration in the light ; those of safranine and those obtained from azo-dyes show more resistance.

ORGANIC COLOURING MATTERS

Organic colouring matters may be either *natural* or *artificial*.

The former are mostly derived from plants (*vegetable colours*) and may be contained in woods (e.g., *campeachy, Brazil wood, sandalwood, yellow wood, fustic*), barks (*quercitron*), roots (*madder, turmeric*), leaves (*indigo, woad*), flowers (*safflower*), fruit (Persian berries) and lichens (*archil*). Far fewer are *animal colours* (*cochineal, kermes*).

The *artificial organic colouring matters* form the large class known as *coal-tar dyes*.

Certain vegetable colouring matters, such as alizarin (from madder) and indigo, are now prepared artificially and are hence considered both as natural and as artificial organic dyes.

The following paragraphs deal especially with the tests and determinations to be made on the principal natural and artificial organic dyes, and among the former are considered certain tanning materials (*q.v.*) which also serve as colouring matters, namely, catechu and gambier.

As regards the identification of colouring matters on textile fibres dyed with them, reference may be made to the chapter on textile fibres.

DYE WOODS AND BARKS AND THEIR EXTRACTS

Dye woods and *barks* are sold in lumps or ground or powdered, or as *dyeing extracts*. The latter are aqueous decoctions of the materials and are met with either as more or less dense *liquids* or *in the dry state* as cakes, irregular or, rarely, crystalline fragments, or powder. They are usually brown or yellowish and they have a sweet taste, almost or quite free from astringency ; they burn with emission of the odour of burning vegetable matter and leave little ash ; they are more or less completely soluble in water and sometimes also in alcohol.

Dyeing extracts may be mixed or adulterated with tanning extracts and may also be adulterated with artificial organic dyes or various inert substances, either organic (molasses, glucose, dextrin, starch, glue) or inorganic (sodium sulphate and other soluble salts, and insoluble substances).

In testing dye woods and barks, these are ground as finely as possible. The moisture and ash are determined on the ground product, and a weighed quantity of the latter is extracted with hot water and the solution made up to the desired concentration for each test, this solution being used for the identification of the product and for the dyeing tests by which the value is established.

In testing extracts, it suffices to dissolve or dilute them with water. The solutions are subjected to the above tests, also to others described below for the detection of adulterations, and to those indicated later for the more important separate extracts. From the commercial point of view, interest attaches also to the specific gravity of liquid extracts, this being measured with a hydrometer and usually expressed in degrees Baumé.

1. Identification of Dyeing Extracts and their Distinction from Tanning Extracts.—The nature of a dyeing wood or extract is recognised, besides by its external characters, by means of certain reactions which are carried out on an aqueous decoction of the wood or on a dilute solution of the extract containing about 0·5% of dry matter. These reactions (*see* later under the separate extracts) refer to the behaviour towards acids and alkalies and especially towards certain metallic salts (alum, stannous chloride, ferric chloride, etc.), with which solutions of the dyeing extracts give coloured lakes.

It is of importance to distinguish the colouring extracts from tanning extracts and to detect addition of the latter to the former.   In general, dyeing extracts have a sweetish and tanning extracts a strongly astringent taste ; as a rule the latter do not give differently coloured lakes with metallic salts (*see* chapter on Tanning Products).   If a solution of the extract of the above-mentioned concentration is treated with one-third of its volume of yellow ammonium sulphide, pure dyeing extracts give a brown coloration and a brown, light, flocculent precipitate, whilst in presence of tanning extracts the colour of the liquid pales and a greyish, milky precipitate is formed.

The above reactions, however—especially with mixtures of different extracts—do not always yield certain results, and in any case comparison should be made with extracts of known origin.

The best results in this direction are obtained by dyeing tests with suitable mordants (*see* later), followed by examination of the colouring matter fixed on the fibre (*see* chapter on Textile Fibres).

2. Moisture.—5 grams of the substance are dried (after evaporation in the case of a liquid extract) at 105° to constant weight.

3. Determination and Examination of the Ash.—From 5 to 10 grams of the extract are weighed in a platinum dish (8–10 cm. in diameter) which is placed in an air-oven and heated slowly to 180°, this temperature being maintained for two hours ; the residue is then carefully incinerated in a muffle.

The ash, especially if fairly large in amount, is tested for mineral adulterations, such as sodium sulphate, alum, sodium chloride, clay, etc.   Sometimes the alkalinity of the soluble ash is required (e.g., to confirm the presence of molasses), this being determined by dissolving the ash in boiling water, filtering and titrating with N/10-sulphuric acid in presence of methyl orange. The alkalinity is expressed as parts of potassium carbonate per 100 of dry matter.[1]

4. Detection of Artificial Organic Dyes.—Dyeing extracts are sometimes " improved " with artificial organic dyes.   Unless these are present in very small quantity, they may be suspected from the odour emitted when the extract is burnt.   Moreover, the colour reactions of dyeing extracts are more or less altered by the presence of artificial dyes.

When shaken with alcohol, ether, benzene, nitrobenzene, etc., dyeing extracts as a rule do not colour these solvents, whereas artificial organic dyes dissolve in some of them and thus colour them.   In some cases the extraction may be effected after the substance has been rendered acid or alkaline.

Artificial organic dyes may also be detected in dyeing extracts by dyeing tests and subsequent examination of the colouring matters thus fixed on the fibre (*see* Textile Fibres).

5. Extraneous Organic Substances.—For the detection of such substances the extract is dissolved in water, precipitated with basic lead

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[1] With extracts to which acid mineral salts have been added as well as molasses, the alkalinity of the ash is of no value.   In this case the potash in the ash should be determined gravimetrically (Savini).

acetate and filtered : if the filtrate exhibits optical rotation and if, either before or after being heated with hydrochloric acid (inversion), it produces marked reduction of Fehling's solution, the presence of glucose or saccharose (molasses) is indicated. A slight reduction by the non-inverted liquid does not, however, indicate with certainty the addition of saccharine substances, since dyeing extracts themselves may contain small quantities of reducing substances.

If the liquid obtained as described above, although not containing sugars, yet exhibits marked dextro-rotation, the presence of dextrin is denoted. If the liquid leaves on evaporation a residue which burns with the odour of nitrogenous matter, the presence of glue is indicated ; this may also be recognised by determining the nitrogen in the extract, which, if pure, does not usually contain more than 1% of nitrogen.

As regards starch, this may be investigated microscopically, best in the residue left after extraction of the dyeing extract with ether and alcohol.

6. Dyeing Value.—The best criterion of the dyeing value of a dyeing extract is obtained by a small *dyeing test*, which is made also on a genuine extract for purposes of comparison. This test is carried out differently with different extracts and according to whether the colour is to be applied to cotton, wool or silk ; most commonly the tests are made with wool.

For the methods of making these tests, *see* under the separate extracts.

1. Logwood Extract

This forms either shining, brownish-black lumps, or a liquid of 10–30° Baumé. There are also on the market : the active principle of logwood (*haematoxylin*), as a powder of crystalline appearance which gives a solution turning red in the air ; certain products (*haematein, haematin*) consisting of the more or less pure colouring matter in brown powder or lumps.

Besides being subjected to the tests indicated for dyeing extracts in general, logwood extract is examined as follows.

1. Qualitative Investigation.—The aqueous solution of logwood extract is deep red if the extract is neutral, reddish-violet if alkaline, or yellowish if acid (extracts containing tanning substances are always acid) ; it is turned reddish-yellow and yellow by acids and reddish-violet and then brown by alkalies.

With an equal volume of stannous chloride, the dilute solution of the extract (about 0·5% of dry matter) gives a violet precipitate if the extract is non-fermented or a dark brown precipitate if the extract is fermented. The same solution gives a bluish-violet precipitate with copper acetate, a blackish-blue precipitate with ferric chloride, and a violet precipitate with alum and then sodium carbonate. With chloride of lime it becomes first reddish-brown and then decolorised.

2. Detection of Tanning Extract.—Besides the tests indicated for extracts in general, the following method (Houzeau's) may be used, especially for detecting chestnut extract : 1 gram of the extract, dried at 100°, is extracted with anhydrous ether, the solvent being then evaporated and the residual extracted matter weighed. This residue is then extracted with absolute alcohol and the alcoholic extract weighed. Since genuine

logwood extracts give about 87% of ethereal extract and about 14% of alcoholic extract, whilst chestnut extracts yield almost nothing to ether and give a far more abundant alcoholic extract, diminution of the ethereal extract and increase of the alcoholic extract would indicate the adulteration. The test may then be completed by separate dyeing tests with the part soluble in ether and that soluble in alcohol, in comparison with similar tests on a genuine extract : especially the part soluble in alcohol will give highly divergent results if the extract is adulterated.

The qualitative test may be confirmed by a quantitative determination of the tannin substances, which occur in far larger proportions in tanning extracts.

3. Detection of Molasses and Sugar.—These may be detected as indicated above for extracts in general (paragraph 5), but more particularly with logwood extract and more exactly as follows (Savini) :

40 grams of a fluid extract or 20 grams of a dry one are weighed, dissolved in 100 c.c. of boiling water and the whole transferred to a 200–220 c.c. flask. 50 c.c. of basic lead acetate solution are added with shaking and the whole cooled if necessary and made up to 220 c.c. (to allow for the volume of the insoluble matter). The solution is shaken well and filtered, 100 c.c. of the filtrate being treated in a 150 c.c. measuring flask with sodium phosphate and sulphate until the excess of lead is precipitated, made up to the mark, mixed and filtered. Part of the liquid is inverted and the polarisation of this and of the non-inverted part measured, the saccharose being then calculated in the ordinary way by Clerget's formula. When necessary the glucose may be determined in another part of the liquid by means of Fehling's solution.

4. Dyeing Test.—To ascertain the actual dyeing value of a logwood extract, the most important test is a dyeing test with wool mordanted with bichromate.

A piece of light woollen tissue weighing about 5 grams is kept for some hours in a 0·5% ammonium carbonate solution, then washed with water and immersed while still moist in 10 c.c. of a solution containing 8 grams of potassium bichromate and 2 grams of concentrated sulphuric acid per litre, diluted with a sufficient quantity of water ; this solution is gently boiled for about half an hour and then allowed to cool away from the light, the material being afterwards removed and without drying immersed in the dye bath. The latter is prepared from 5 grams of extract, which is dissolved in hot water (or, in the case of wood, from 20 grams of the ground wood, which is extracted with hot water), the solution being filtered through cloth, the latter well washed, and the liquid made up to a litre. According as a light or dark tint is required, 10 or 20 c.c. of the solution thus prepared are taken and diluted with a sufficient quantity of water, the mordanted woollen material being immersed and the liquid heated to boiling for half an hour ; the material is then removed from the bath, washed in flowing water and dried in the air.

The test is repeated under identical conditions with an extract (or wood, as the case may be) taken as a standard. If the dyeing with the extract under examination is the paler, another test is made with an increased

quantity of the extract solution ; a better plan consists in preparing a
scale of comparison, 20, 18, 16, 14 . . . c.c. of the solution of the standard
extract being used for 5 grams of wool, the colours thus obtained being used
for matching that given by 20 c.c. of the solution of the extract under
examination.   That weight of the extract being tested which corresponds
with 100 parts of the one chosen as standard is then readily calculated.

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Good logwood extract usually contains 40–45% of water if liquid or 9–12%
if solid ; it should not contain added extraneous substances, especially sugar
or low products in the dry extracts or molasses in the liquid extracts.   In
genuine extracts there is no saccharose and the alkalinity of the ash varies
from 0·4 to 0·5 gram (expressed as potassium carbonate) per 100 grams of dry
matter.

2. Red Wood Extract

Extract of red wood or Brazil wood forms either brittle, opaque lumps
or masses of a garnet-red colour, or a more or less dense, reddish-brown
liquid.

In addition to the tests and determinations already indicated for all
dyeing extracts, the following tests are made in this case.

1. Qualitative Tests.—The solution of the extract is reddish-yellow
with a more or less brown tint ; by acids it is turned to orange and rendered
slightly turbid and by alkalies crimson.   Stannous chloride gives a red
precipitate with the solution, ferric chloride a reddish-brown precipitate
and alum and then sodium carbonate a red precipitate.   The solution of
the extract is decolorised by chloride of lime and also by sodium sulphite
(difference from red sandalwood and the like).

2. Colorimetric Test.—A solution of 2 grams of pure copper sulphate
in a litre is prepared and one of a standard extract (or of pure haematoxylin)
of such concentration that it contains 1 gram of dry substance per litre ;
1 c.c. of the latter solution, diluted with 10 c.c. of water and mixed with
1 c.c. of the copper solution, is heated to boiling and then diluted with
water to 100 c.c. ; the liquid thus prepared is used as a standard.

Next a solution of the extract under investigation containing 1 gram
of dry matter per litre is prepared and 1 c.c. of this treated with water
and the copper solution in the manner described above.   The colours of
the two liquids are then compared, but this should be done not later than
15 minutes after their preparation.

3. Dyeing Test.—Wool is mordanted by boiling it with 3% of its
weight of potassium bichromate dissolved in a sufficient amount of water
(without sulphuric acid).   It is then dyed with a solution of 5 grams of
the extract per litre (or, in the case of a wood, with the decoction obtained
by extracting 20 grams of the wood and making up to a litre), using 10
c.c. for every gram of wool and boiling for half an hour.   The colour obtained
is compared with that obtained by operating similarly with a standard
extract, with which a scale of colours may be prepared in the same way as
with logwood extract.

If a dyeing test with cotton is required, this is mordanted by boiling with 5% aluminium acetate solution and then exposed for some time to hot, moist air; for each gram of cotton 20 c.c. of the extract solution are used.

3. Yellow Wood Extract

In the dry state this forms brownish-yellow, opaque masses of waxy lustre; in the liquid state it is more or less dense and of a brownish-yellow colour.

Besides the tests indicated for extracts in general, the following are carried out.

1. Qualitative Tests.—The solution of this extract is yellow and with acids becomes paler and then gives a yellow precipitate, whilst with alkalies it becomes darker and gives an orange-brown precipitate. The solution also gives a yellow precipitate with stannous chloride, a deep olive green precipitate with ferric chloride and a pale yellow precipitate with alum and then a few drops of sodium carbonate solution. With chloride of lime it first turns brown and then colourless, a brownish-yellow precipitate settling.

2. Dyeing Test.—Wool is mordanted with 10% of its weight of alum dissolved in sufficient water, boiling for three-quarters of an hour and then washing. The wool thus mordanted is dyed; for each gram of wool, 10 c.c. of a solution of the dyeing extract containing 10 grams of dry matter per litre are used (or the decoction obtained by extraction of a corresponding amount of a wood), heating at 80–90° being continued for three-quarters of an hour. The colour obtained is compared with that given by a standard extract; a scale of colours may be conveniently prepared from the latter by using 10, 9, 8 . . . c.c. of the solution of the concentration mentioned for each gram of wool.

4. Quercitron Extract

This forms either dark brown, shining lumps or a more or less dense brown liquid. Under the names of *flavine* and *quercetin*, products are sold which are obtained by chemical processes from quercitron bark and represent the more or less pure colouring matter in the form of yellow or brown powder or paste.

In addition to the general tests already indicated, the following are made in this case.

1. Qualitative Tests.—The solution of quercitron extract is yellow and gives a pale, yellowish-brown precipitate with acids and turns brown with alkalies. Stannous chloride gives a yellow precipitate, ferric chloride an olive green precipitate, alum a light, yellow precipitate and a filtrate with greenish fluorescence, and copper acetate a greenish-yellow precipitate. With chloride of lime the solution becomes decolorised and yields a yellow precipitate.

As regards flavine and quercetin, these dissolve more or less completely in ammonia and in alkalies to golden yellow solutions, and the ammoniacal solution turns brown in the air; their alcoholic solution is coloured brownish-

green by ferric chloride, whilst lead acetate gives a brick-red precipitate ; the filtrate from the precipitate obtained in aqueous solution with alum is colourless and non-fluorescent.

2. Dyeing Test.—Wool is mordanted by boiling with 1·5% of tin salt and 3% of oxalic acid dissolved in sufficient water and is then washed and dyed, 20 c.c. of a solution containing 10 grams of extract per litre (or the decoction obtained from an equivalent quantity of bark) being used for each gram of wool. For purposes of comparison, use is made of a product chosen as a standard, a colour scale with different quantities of the solution being prepared as indicated for other extracts.

<p style="text-align:center">*_**</p>

A *good flavine* should have a colouring power about sixteen times as great as that of quercitron bark.

INDIGO

Both *natural* and *artificial* or *synthetic* indigo are now sold.

Natural indigo is in more or less bulky lumps, that of good quality being light, of a deep azure colour and with metallic coppery reflection, especially when scratched with the nail; its fracture is homogeneous and opaque. Indigo of poor quality is, however, heavy and tends in colour towards reddish-violet, while the lowest qualities are greyish or greenish blue.

Artificial indigo is sold as a deep azure powder with coppery reflection, or more commonly as a moist paste.

Natural indigo, besides *indigotin* or *indigo blue*, which is the principal blue colouring matter of indigo, contains also: *indirubin* or *indigo red*, *indigo brown* and gelatinous substances (*indiglutin*) and may be contaminated more or less with mineral substances (sand, silicates, salts of calcium, potassium, magnesium and iron). Artificial indigo is, however, composed (with the exception of water in the pasty product) of almost pure indigotin.

Indigo, especially the natural product, may be adulterated with mineral substances (sand, clay, slate, brickdust, barium sulphate, chalk, graphite), starch, dextrin, gum, resin, dyeing extracts, Prussian blue, etc.

The examination of natural indigo, with the object of ascertaining its purity and adulterants and of determining its dyeing value, comprises mainly the tests and determinations indicated below. Synthetic indigo is usually examined only as to its water (if in paste) and ash contents, the indigotin being determined and a dyeing test carried out if required.

1. Specific Gravity.—This is determined with a picnometer, using alcohol or benzine as liquid.

2. Water.—From 1 to 2 grams of the finely powdered indigo are dried at 100–105° to constant weight.

3. Determination and Examination of the Ash.—From 1 to 2 grams of the indigo (the dry residue from the preceding determination may be used) are incinerated in a platinum crucible. If the ash is large in amount,

it may be analysed qualitatively to detect mineral substances present as impurities or adulterants.

4. Extraneous Organic Matter.—The powdered indigo is mixed to a paste with a little water : if it gives a gluey or mucilaginous mass, gum or dextrin is present. If a little more water is added and the mass filtered, the filtrate may be tested for these substances.

A little of the indigo is treated with nitric acid, water and then potassium iodide solution being added : a blue coloration indicates the presence of starch.

A little of the substance is treated with alcohol and filtered, the solution being tested for resins.

The substance is treated with oxalic acid solution and filtered : a red filtrate indicates the presence of logwood extract, which may be confirmed by the violet-blue precipitate formed by addition of alum and sodium carbonate.

A portion of the substance is boiled with sodium hydroxide solution, diluted and filtered, the filtrate being acidified and treated with ferric chloride : a blue precipitate shows that the indigo contains Prussian blue.

5. Detection of Indigo Red and Brown.—A few grams of the finely powdered indigo are treated with dilute hydrochloric acid and filtered ; the indigo gum and part of the mineral matter pass into solution. The insoluble residue is washed with water, treated with dilute sodium hydroxide solution and filtered : the solution contains the indigo brown. The new residue, insoluble in sodium hydroxide, is washed, dried and extracted with boiling alcohol : the indigo red dissolves, whilst the indigotin and part of the mineral substances remain undissolved.

6. Determination of the Indigotin.—Many methods have been suggested for the determination of indigotin in indigo, the two following volumetric methods being among those most commonly used.

(*a*) PERMANGANATE METHOD (Rawson's). This is based on the oxidising action of potassium permanganate on indigotin and its sulphonic derivatives. 1 gram of the indigo, finely powdered and dried at 100°, is mixed with an equal amount of glass powder, 20 c.c. of pure sulphuric acid ($D = 1.845$) being carefully stirred in to the mixture, which is then heated for an hour on a water-bath at 90°, allowed to cool and made up to a litre with water. The liquid is filtered and 50 c.c. of the filtrate ($= 0.05$ gram of the substance) diluted in a porcelain dish with 250 c.c. of water and titrated with N/50-potassium permanganate until it passes through a greenish tint to pale yellow.

1 c.c. of the permanganate solution corresponds theoretically with 0.00131 gram of indigotin, but practically with a larger quantity (about 0.0014–0.0015 gram) ; it is therefore preferable to determine the titre of the permanganate directly by means of a standard solution prepared as above with 1 gram of pure indigotin.

This method gives rather high results, especially if the indigo contains much indirubin, indigo brown or iron salts, or if it has been fraudulently mixed with oxalic acid to falsify the result of the titration.[1]

[1] *Ann. de chim. analyt.,* 1902, p. 256.

In such cases it is well, in order to eliminate the causes of error, to proceed as follows : the indigo is dissolved in sulphuric acid as described above, made up to a litre and filtered. 50 c.c. of the filtrate are diluted with as much water and then mixed with 32 grams of sodium chloride and left at rest for two hours, the sodium indigotinsulphonate being thus precipitated. The precipitate is filtered off, washed with about 50 c.c. of saturated sodium chloride solution, and then redissolved in hot water containing 1 c.c. of sulphuric acid ; the solution is diluted with water to 300 c.c. and titrated with permanganate as described above. To allow for the small amount of indigotin remaining dissolved in the salt solution, 0·0008 gram is added to the weight of indigotin found in the 50 c.c. of solution used.

The sources of error mentioned above may also be eliminated by first treating the indigo with dilute hydrochloric acid, then washing with hot water and afterwards extracting with a mixture of alcohol (4 parts) and ether (1 part). It is then treated with sulphuric acid and titrated as in the method first described.

(b) HYDROSULPHITE METHOD. This is based on the decolorisation of indigotin by means of sodium hydrosulphite.

Reagents. 1. Hydrosulphite solution prepared by dissolving 3–4 grams of pure powdered sodium hydrosulphite in water with addition of 3 grams of sodium hydroxide and making the volume up to a litre. This solution should be kept away from the light and air (it is convenient to cover it with a layer of petroleum) and as it is unstable, its titre should be determined immediately before it is used.

2. A solution of indigotin or of ammoniacal copper sulphate to determine the titre of the hydrosulphite ; these are prepared thus :

(a) Indigotin solution. Exactly 1 gram of pure, dry indigotin is dissolved with sulphuric acid in the manner used with the permanganate method (*q.v.*) and made up to a litre : 1 c.c. of this solution contains 0·001 gram of indigotin.

(b) Ammoniacal copper sulphate solution. 1·904 gram of pure, minutely crystalline copper sulphate is dissolved in water, 100 c.c. of concentrated ammonia being added and the volume made up to a litre : 1 c.c. of this solution corresponds with 0·001 gram of indigotin.

Apparatus. In titrating the hydrosulphite solution it is absolutely necessary to avoid all contact with the air. All such titrations must therefore be carried out in a special apparatus like that represented in Fig. 67, this comprising :

1. A Mariotte's bottle *A*, containing the hydrosulphite solution covered with a layer of petroleum and closed with a stopper traversed by two glass tubes bent at right angles ; one of these communicates by way of a rubber tube with a source of hydrogen or illuminating gas (*G*) and the other, fitted with a short rubber tube which terminates in a pointed glass tube and is provided with a clip *p'*, can be put into communication with the external air.
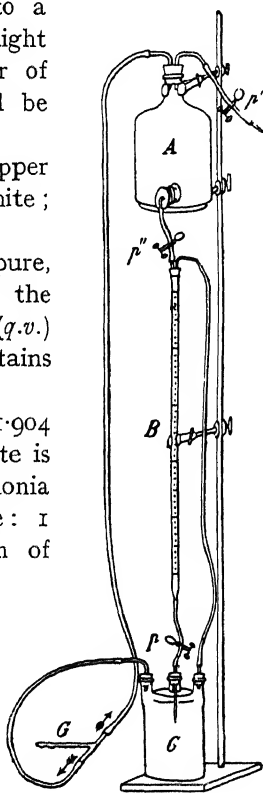
FIG. 67

2. A 50 c.c. burette B closed by a rubber stopper, traversed by two glass tubes, one of which communicates through the clipped rubber tube p'' with the side tube of the Mariotte's bottle A. At its lower end the burette is connected with a clipped rubber tube p terminating in a tapered glass tube passing through a rubber stopper.

3. A 3-necked Woulff's bottle C of about 250 c.c. capacity, in which the titration is carried out. One of the lateral necks communicates with the gas supply G, while the other is joined through a rubber tube with the upper end of the burette B ; the central opening of the bottle may be closed by an ordinary rubber stopper or by the stopper traversed by the glass tube connected with the bottom of the burette, the point of this tube being at about the middle of the bottle.

Titration of the hydrosulphite solution. 50 c.c. of the copper or indigotin solution($= 0.05$ gram of indigotin) are introduced into the Woulff's bottle C, the middle orifice of which is closed by a rubber stopper, the one carrying the tube from the burette being left free. The clips p and p' are opened and the hydrogen or illuminating gas allowed to pass into the Woulff's bottle C and the burette B and, on the other side, into the Mariotte's bottle A, the air being displaced from A, B and C.

When the air is expelled, the clips p and p' are closed and p'' opened to allow the hydrosulphite solution to pass into the burette B. When this is full the clip is closed again and the height of the solution adjusted, care being taken that the liquid fills the rubber tube and the glass jet. The stopper in the central neck of the Woulff's bottle is then carefully and rapidly replaced by that carrying the glass jet of the burette and the titration then carried out.

The hydrosulphite is added to complete decolorisation of the liquid when the copper solution is used, or to the passage from greenish to pale yellow with indigotin solution : the amount of indigotin corresponding with 1 c.c. of the hydrosulphite solution is thus found.

Procedure. 1 gram of the indigo, powdered and dried at 100° and mixed with as much glass powder, is treated with 20 c.c. of sulphuric acid in the manner indicated for the permanganate method and the volume made up to a litre. 50 c.c. of the filtered solution ($= 0.05$ gram of the substance) are introduced into the Woulff's bottle, the air then displaced by gas and the titration with hydrosulphite carried out as before. The colour passes first to green and then to a more or less pale yellow, according to the quality of the indigo ; the addition of hydrosulphite is stopped when the last trace of green disappears.

If the indigo contains much indirubin, when the indigotin (which is reduced first) is decolorised the colour passes to reddish-violet, this denoting that the titration of the indigotin is complete. If addition of hydrosulphite is continued, the indirubin also undergoes reduction and the colour passes to yellow ; thus, with a little practice, the indirubin may also be determined with fair approximation.

The presence of ferric salts will disturb the titration, but such salts are seldom found in appreciable amount in indigo.

EXAMPLE : Suppose 30 c.c. of the hydrosulphite solution are required

to decolorise 50 c.c. of the standard indigotin or copper solution ($=0 \cdot 05$ gram of indigotin) ; the titre of the hydrosulphite will be $0 \cdot 05 : 30 = 0 \cdot 001667$, i.e., 1 c.c. of the hydrosulphite $= 0 \cdot 001667$ gram of indigotin.

If then 50 c.c. of a solution of the indigo under investigation ($= 0 \cdot 05$ gram of substance) require $20 \cdot 6$ c.c. of hydrosulphite, the percentage of indigotin will be given by $\dfrac{0 \cdot 001667 \times 20 \cdot 6 \times 100}{0 \cdot 05}$ or, more shortly, by $\dfrac{20 \cdot 6 \times 100}{30} = 68 \cdot 67\%$.

7. Colorimetric Test.—$0 \cdot 3$ gram of indigo is dissolved in the hot in 5 c.c. of pure concentrated sulphuric acid, a similar solution being also prepared from $0 \cdot 3$ gram of pure indigotin or of a standard indigo. When the indigo is dissolved, the volume is made up to 3 litres with water, 10 c.c. of each solution being compared in the Duboscq colorimeter. The relative colours are thus determined.

If the colour of the indigo solution corresponds with that of the standard indigo (or indigotin) solution after 10 c.c. of the latter have been diluted with 2 c.c. of water, the colouring power of the indigo will be 10/12 or $83 \cdot 3\%$ of that of the standard indigo (or indigotin).

8. Dyeing Test.—1 gram of pure indigotin is dissolved with 20–25 grams of pure concentrated sulphuric acid and the liquid diluted with water to a litre. Into 20 beakers each containing 500 c.c. of water are poured 1, 2, 3, . . . 20 c.c. of this solution and into each liquid are introduced 5 grams of woollen yarn or thin fabric, previously defatted by immersion in a 1% ammonium carbonate solution at 30–40° and washed in running water. The different tests are heated to boiling, which is maintained for three-quarters of an hour ; the wool is then removed from the bath—which is almost decolorised—allowed to cool, washed in running water and dried in the shade. This scale of 20 standard colours keeps unchanged indefinitely away from the light and air.

With a commercial indigo, 1 gram is dissolved with sulphuric acid as above and the solution made up to a litre. With 20 c.c. of this solution, diluted with 500 c.c. of water, 5 grams of wool (yarn or fabric) are dyed in the same conditions as before and are then compared with the scale.

If, for example, the colour obtained with the indigo under examination coincides with colour No. 13 of the scale, 20 c.c. of the indigo solution correspond with 13 c.c. of the pure indigotin solution, its dyeing value being thus 65% of that of pure indigotin.

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Natural indigo has a specific gravity varying from $1 \cdot 1$ to $1 \cdot 5$ (usually $1 \cdot 3$–$1 \cdot 45$) and diminishes as the richness in indigotin increases and the proportion of mineral matter diminishes. Good natural indigo mostly contains 3–7% of water and 2–10% of ash, but poor qualities may contain as much as or even more than 25% of ash. The indigotin content may be as low as 20% or more than 90% ; the best Bengal qualities contain 75% or more, but the more common grades usually show 50–70%. Madras indigo contains 20–40% or, rarely, 50% of indigotin, while that from Java may contain 70–80%, and that from Guatemala usually 45–60%.

Indigo red is found in the Indian and Guatemala products to the extent of 1–8% and in that from Java in much larger quantity ; the amount of indigo brown may reach 5%, and that of indigo gum 4%.

Powdered *artificial indigo* usually consists of almost pure indigotin (about 98%) ; in the paste its concentration varies (usually 20%).

INDIGO CARMINE

Indigo carmine commonly consists of indigotindisulphonic acid or its sodium salt, which is sold as a moist paste or in blue balls or lozenges with reddish reflection. Indigotinmonosulphonic acid (*indigo purple*) is little used. Pure indigo carmine is completely soluble in water, from which it is reprecipitated by addition of sodium chloride. Commercial carmines of low quality leave a more or less abundant greenish residue insoluble in water.

The examination of indigo carmine includes the determination of the acidity and tests for artificial organic dyes (*see* below), also determination of the colouring substance and the colorimetric and dyeing tests, these being carried out as with indigo (*q.v.*) without previous treatment with sulphuric acid (for the determination of the colouring matter the permanganate method is especially used).

1. Acidity.—1 gram of the carmine is dissolved in 100 c.c. of water and then treated with 32 grams of pure sodium chloride, shaken and filtered, the precipitate being washed with salt water. The acidity is determined in the liquid by titrating with decinormal KOH in presence of phenolphthalein, the result being calculated as sulphuric acid.

2. Artificial Organic Dyes.—Indigo carmine may be adulterated with artificial organic dyes, especially aniline blue. If silk is dyed with an acidified solution of the carmine and then washed and boiled with water, the fibre will become colourless if the carmine is pure, but remains blue if aniline blue is present.

Also by oxidising the carmine solution with permanganate for the determination of the indigotin, many artificial organic dyes may be detected; thus, pure indigo carmine solution remains yellow, whereas it may be bluish, violet, grey or reddish in presence of artificial organic dyes.

ALIZARIN

Natural alizarin of madder is now scarcely ever used, commercial alizarin being obtained artificially. It forms either a wet, ochre-yellow paste, usually containing about 20% of solid matter (sometimes as much as 40 or 60%) or dry powder or lumps.

Of the different commercial qualities of alizarin, some are composed of almost pure *alizarin* (dihydroxyanthraquinone), others of mixtures of this with *flavopurpurin* and *anthrapurpurin* (isomeric trihydroxyanthraquinones), and others almost solely of one or other or both of the two latter substances. Another isomeride of these, *purpurin*, is also a commercial product.

Besides these, use is also made (especially for dyeing wool), under the name of *alizarin red*, of the sodium salts of the respective sulphonic derivatives, which form orange-yellow powders.

Commercial alizarin may be contaminated with anthraquinone and its derivatives devoid of tinctorial value, such as hydroxyanthraquinone and certain dihydroxyanthraquinones (anthraflavic and isoanthraflavic

acids) isomeric with alizarin ; it may also be mixed or adulterated with starch, dextrin, glycerine, emulsive oils and mineral salts.

Examination of alizarin comprises mainly the following tests and determinations.

1. Qualitative Reactions.—Alizarin is insoluble in water, but soluble in boiling alcohol or in ether ; it dissolves in sodium hydroxide solution, giving a solution which is violet-blue for pure alizarin, violet for anthrapurpurin, purple-red for flavopurpurin, and red for purpurin. The sulphonic derivatives are soluble in water and give violet alkaline solutions.

The presence of monohydroxyanthraquinone may be detected by dissolving a little of the substance in sodium hydroxide solution, treating the alkaline solution in the hot with baryta water and filtering : if the filtrate is red and gives a flocculent yellow precipitate when acidified with hydrochloric acid, monohydroxyanthraquinone is present.

Anthraflavic and isoanthraflavic acids are detected by treating a little of the substance suspended in boiling water with barium hydroxide and filtering the liquid : in presence of the above acid the filtrate is red and gives a yellow precipitate when neutralised with hydrochloric acid.

2. Water.—This is determined more especially in alizarin paste. 5 grams of the substance are weighed in a dish and heated in an oven at 100° to constant weight ; loss of weight represents water.

If the alizarin has been badly washed, the dried colouring matter shows a saline ring round it.

3. Ash.—The dry residue from the determination of the water is incinerated and the ash weighed. If this exceeds 1%, adulteration with mineral matter is probable, this being confirmed by qualitative analysis of the ash. Such analysis is useful in any case to detect the presence of heavy metals (especially iron), which may be introduced during the manufacturing processes and are harmful in the dyeing. The ash of alizarin consists normally of sodium or calcium salts.

4. Various Anthraquinone Derivatives.—These may be determined approximately in commercial alizarin by the following method (Benedikt and Knecht) :

A certain quantity (5–10 grams) of the sample is dissolved in sodium carbonate solution and filtered. The anthraquinone and monohydroxyanthraquinone remain on the filter and after suitable washing and drying are weighed ; they may be separated by means of dilute sodium hydroxide solution, which dissolves only the monohydroxyanthraquinone.

The filtrate is treated with hydrochloric acid and the precipitate obtained boiled with milk of lime, which dissolves the anthraflavic and isoanthraflavic acids with red coloration. The solution is filtered and the filtrate precipitated with hydrochloric acid, the precipitated anthraflavic and isoanthraflavic acids being filtered off, washed, dried and weighed.

The lime lake remaining behind may contain alizarin, anthrapurpurin and flavopurpurin. It is treated with dilute hydrochloric acid and then shaken with ether, which dissolves these colouring matters, the ethereal layer being separated and evaporated and the residue dried at 100° and weighed.

In this residue the alizarin and the two trihydroxyanthraquinones (flavopurpurin and anthrapurpurin) may be estimated approximately (according to Schunck and Römer) by heating the residue between clock-glasses at 130–150°, at which temperature only the alizarin volatilises and sublimes. If the residue is then heated at 170°, the flavopurpurin and the anthrapurpurin also sublime (the former in reddish-yellow needles and the latter in rhombic crystals) ; these may be separated by means of boiling benzene, which dissolves only the flavopurpurin.

5. Extraneous Organic Substances.—To detect glycerine and dextrin, the substance is mixed with water, the insoluble matter allowed to settle, the liquid filtered, the filtrate evaporated and the residue examined as to its external characters, polarisation, behaviour when heated, etc. Starch is detected microscopically, and fatty oils by extracting the substance with ether and examining the ethereal extract.

6. Dyeing Test.—Alizarin is fixed on fibres by means of mordants and, according to the nature of the latter and of the fibres, produces colours varying from yellowish-red to brownish-red and to more or less bluish violet.

For the dyeing test it is hence necessary to vary the procedure in accordance with the fibre to be dyed and the colour desired. In general, comparative tests are made with a standard alizarin and that under examination, using strips of cotton material (calico) mordanted in different ways, namely :

(a) With concentrated aluminium acetate solution.

(b) With dilute aluminium acetate solution.

(c) With concentrated ferric acetate solution.

(d) With dilute ferric acetate solution.

(e) With a mixture of concentrated solutions of the two above acetates.

(f) With a mixture of dilute solutions of the two acetates.

For each mordant solutions of fixed concentration are employed, definite volumes being used for a certain time and at a certain temperature for the same amount of cotton.[1]

Half a gram of alizarin paste is mixed with a litre of ordinary water at 40° ; strips of mordanted cotton are then immersed in this bath which is heated on a water-bath, the temperature being raised to 75° in about 1½ hour and then to 90° in about half an hour. The cotton is then removed, washed with cold water, immersed in a 0·2% white soap bath for half an hour, washed in running water and dried.

In this way the colour and intensity given by the alizarin with various mordants may be judged.

For Turkey red dyeing, the fabric is immersed in a tepid 5% emulsive oil

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[1] Strips of cotton material are sold which are mordanted with various mordants in parallel zones, so that the different tints may be compared on a single piece of stuff. One such strip is about 20 cm. wide and is divided into five zones, which are treated with different mordants (iron, strong and weak ; aluminium, strong and weak ; iron and aluminium together) and separated by non-mordanted lines. It is useful for testing the various natural organic colouring matters, mordant dyes in general, and tanning materials ; the latter give, with iron mordants, tints varying from black to brown or green.

solution, then dried, mordanted with aluminium acetate, again dried and then transferred to the dye bath, to which a little sulphoricinate is added. The fabric is afterwards exposed to steam for an hour and then treated in the soap bath.

CATECHU, GAMBIER

These two substances, composed of the evaporated and dried aqueous extracts of certain plants, may be included among the colouring matters and also among the tanning materials, with reference to either their composition or their uses.

Catechu forms brittle, reddish-brown masses, with a shining or opaque fracture and an astringent bitter and then sweetish taste.

Gambier is sold (1) in small cubical cakes of a greenish or yellowish grey colour when fresh, but soon turning brown outside while remaining yellowish internally, or (2) in irregular, brown lumps. It is friable and porous, with an earthy fracture, its taste being astringent bitter and then sweet.

Of similar appearance to these products is *kino*, which is the condensed juice flowing from certain trees and forms brittle, shining, deep-red lumps ; it has a very astringent taste and, unlike catechu and gambier, dyes the saliva red.

Catechu and gambier have catechu-tannic acid and catechin for their essential components. They may be adulterated with mineral matter (earth, ochre, clay, sand), starch, dextrin, extraneous tanning materials and dried blood.

Their examination comprises especially certain qualitative tests for the identification of the product and for the detection of adulteration, and a dyeing test ; sometimes certain quantitative determinations are required. The analytical methods followed are indicated below.

1. Qualitative Tests and Distinction of Catechu from Gambier.— Catechu is almost completely soluble in boiling water ; hot alcohol dissolves about 85–90% of it and ether 28–50%. The aqueous solution gives a brownish-green precipitate with ferric chloride ; the very dilute alcoholic solution is coloured green by the same reagent, the coloration changing to purple on addition of ammonia.

Gambier dissolves in hot water and is largely reprecipitated on cooling ; its dilute solution is coloured green by ferric chloride.

Kino dissolves in water to a red liquid ; with acids, especially in the hot, the aqueous solution gives a reddish precipitate and with ferric chloride a dirty green one.

To distinguish catechu from gambier, the substance is treated with 30% acetic acid or with 10% soda solution and the insoluble residue examined under the microscope : if this consists of fragments of woody fibre the product is catechu, whereas if it is formed of parenchymatous cells and hairs with curved and dotted base, i.e., of leaf elements, the product is gambier.

Another test is as follows : 3 grams of the substance are dissolved in 25 c.c. of water and the solution, treated with a little dilute caustic potash

solution, shaken with 50 c.c. of petroleum ether; if, when the two layers have separated, the petroleum ether has not changed sensibly, the product is catechu, whereas if it has assumed a marked green fluorescence, the product is gambier.

2. Water.—5 grams are dried at 105° to constant weight.

3. Determination and Examination of the Ash.—The residue from the preceding determination is incinerated. A large amount of ash may indicate addition of extraneous mineral substances, the nature of which may be determined by qualitative analysis of the ash.

4. Extraneous Organic Matter.—The presence of starch and dextrin may be recognised in the manner indicated for dyewood extracts.

Addition of extraneous tanning materials (*see* chapter on Tanning Substances) is indicated by the fact that a very dilute alcoholic solution, obtained in the cold and filtered, is coloured more or less intense black rather than green by ferric chloride.

Addition of dried blood is detected by extracting the product with alcohol in the hot and heating the dried insoluble residue in a test-tube : if ammoniacal vapours are emitted, the presence of blood is indicated.

5. Dyeing Test.—10 grams of cotton or wool are dyed with 10% of catechu or gambier with or without addition of 1% of copper sulphate, a litre of water being used with wool or half a litre with cotton. The bath is kept boiling for an hour and is then left to cool for three hours, after which the fibre is withdrawn from the bath, pressed and immersed for half an hour in a 2% potassium bichromate bath at 80°, washed in running water and dried. The resulting colour is compared with that obtained under identical conditions with a standard product.

<p style="text-align:center">*_**</p>

Catechu and *gambier* usually contain 12–25% of water, 2–5% of mineral matter, 24–48% of catechu-tannic acid and 2–12% of catechin.

Kino has a very variable composition and is usually richer in tannin than the preceding.

COCHINEAL AND CARMINE

1. Cochineal

Cochineal consists of the dried body of an insect, which forms a dark brown granule with or without a powdery, white covering.

It is often adulterated with cochineal exhausted of its colouring matter and then dried, or moistened with solutions of dyeing extracts (especially red wood) and is frequently mixed with talc, gypsum, or heavy spar. It is sometimes mixed also with leaden fragments or filings. The tests to be made are as follows :

1. Mineral Matters.—5 grams of the substance are incinerated and the ash weighed. If this is large in amount, addition of inorganic matter may be suspected and the ash qualitatively analysed.

Certain mineral substances may be separated and recognised by shaking the cochineal with water and examining the deposit which settles.

2. Detection of Red Wood Extract.—A dilute aqueous decoction of the substance is treated with lime water : the colouring matter of the cochineal separates as a violet precipitate ; if the liquid remains coloured, the presence of red wood is indicated.

3. Determination of the Colouring Matter.—This determination is made (according to Liebermann) by powdering the substance and extracting a given weight (2 grams) with boiling water, the liquid being treated with lead acetate and the precipitate formed collected on a tared filter, washed, dried at 100° and weighed ; it is then incinerated in a porcelain crucible and the ash weighed. The difference between the weight of the dried precipitate and that of the ash represents approximately the colouring matter of the cochineal.

4. Dyeing Test.—1 gram of the powdered cochineal is boiled repeatedly with water, all the solutions obtained being united and made up to a litre. For each gram of woollen fabric, 100 c.c. of this solution is used, this being diluted with water with addition of 3% of oxalic acid and 1·5% of tin salt (referred to the weight of the fabric).

The wool, after being wetted, is immersed in this bath, which is heated so as to arrive in about half an hour at the boiling point, this being maintained for a further half-hour ; the wool is then washed and dried. The colour obtained is compared with those furnished under identical conditions by a standard product, from which a sale of colours may conveniently be prepared by using 100, 90, 80 . . . c.c. of the solution per gram of wool.

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A *good cochineal* should not leave more than 1% of ash and, if not partially exhausted, should contain 8–10% of the colouring matter.

2. Carmine

The colouring matter of cochineal, precipitated from its solution by means of a weak acid or an acid salt (alum), constitutes *cochineal carmine* or *carmine* proper. This colour is sold in red powder, small cakes or lozenges.

Its most frequent adulterations are with starch, clay, ochre, talc, chalk, minium and lakes of artificial organic dyestuffs (e.g., that of eosin with lead and alumina, of peonin or corallin with baryta, or of Biebrich's scarlet with oxide of tin).

The following tests and determinations are made on carmine.

1. Qualitative Tests.—Carmine is insoluble in water, alcohol or ether. With acids it gives a yellowish-red coloration. In ammonia solution it is completely soluble with an intense red coloration. In potassium hydroxide solution it dissolves to a purple-violet liquid. It is decolorised by chloride of lime but not by sodium sulphite. It burns, emitting an odour of nitrogenous matter and leaving little ash.

2. Determination and Examination of the Ash.—5 grams of the substance are incinerated in a porcelain crucible and the ash weighed and then investigated qualitatively.

3. Extraneous Matter in General.—The substance is treated with dilute ammonia solution : pure carmine dissolves completely, whereas that

mixed with extraneous substances leaves an insoluble residue. Starch may be detected in this residue either microscopically or by means of iodine solution.

4. Lakes of Artificial Organic Dyestuffs.—Of the presence of these lakes an indication is usually obtained by burning the substance : pure carmine emits a distinct odour of nitrogenous material, whilst in presence of artificial organic dyes the odour characteristic of the latter is also produced (in particular, the odour of bromine in presence of eosin and that of phenol in presence of peonin or corallin). The presence of baryta, lead oxide or tin oxide (in marked quantity) in the ash also indicates adulteration with coloured lakes. The presence of the latter modifies the reactions referred to in paragraph 1 (above). For certain artificial organic dyestuffs the following tests may be applied :

Eosin is detected by treating the carmine with dilute sulphuric acid, shaking with ether and evaporating the ethereal solution : the eosin may then be identified in the residue.

Biebrich's scarlet is recognised by boiling the substance with ammonia : in presence of this colouring matter the liquid assumes an orange-red tint, whilst with pure carmine a purple-red liquid is obtained.

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The *ash* of genuine *carmine* usually varies from 5 to 9% and consists mainly of alumina and lime, with small proportions of magnesia, alkalies and phosphoric acid ; often, however, it contains traces of copper and tin oxides derived from the vessels used in its preparation.

The *colouring matter* is contained in carmine to the extent of 30–65%, but more commonly 45–56%.

ARTIFICIAL ORGANIC COLOURING MATTERS

These (commonly termed *coal-tar colours*) are classified, according to their chemical constitution and to the atomic groupings characteristic of each colouring matter, into various groups, the principal ones being :

Nitro-colouring matters, which are not numerous and include principally yellow and orange colours.

Azoxy- and *hydrazo-colouring matters*, which are also not numerous and mostly yellow or orange.

Azo-colouring matters, a very important and numerous class, including different colours.

Quinonoxime derivatives or *nitroso-colouring matters*, which comprise few colours, mostly greens and browns.

Oxyketonic-colouring matters or *anthracene derivatives*, an important and large group.

Di- and *tri-phenylmethane derivatives*, to which various colouring matters, including the so-called aniline colours, belong.

Phthaleins or *pyronine* or *pyrone derivatives*, usually red or violet, and related to the preceding group.

Quinoniminic colouring matters, divided into the sub-groups of *indo-*

phenols, *oxazines* and *thiazines*, and *azines*, and containing some important dyestuffs.

Quinoline and *acridine derivatives*, which are not very numerous and are mostly yellow, orange or red.

Thiobenzenyl- or *thiazole-colouring matters*, which are yellow and form a small group.

Indigo and thioindigo group or *indigoids*, increasingly numerous and important.

Sulphur colouring matters, which have now acquired great importance.

In practice, artificial organic dyestuffs are more commonly divided, according to their behaviour towards textile fibres and towards certain reagents, into : basic, acid, substantive (direct), mordant (adjective), vat, sulphur and developed.

Basic colouring matters are those the solutions of which are decolorised by mineral acids and give a coloured precipitate with tannin (best in presence of sodium acetate). When acidified with sulphuric acid and shaken with ether, their solutions give up nothing to the solvent. They dye animal fibres in a neutral bath or one faintly acid with acetic acid, without a mordant, and they dye cotton in a tannin bath. Mineral acids remove them completely from the fibres on which they are fixed.

Basic colouring matters are usually sold as salts—chlorides, sulphates, nitrates, acetates, oxalates or double salts with zinc or ferric chloride.

Acid colouring matters give solutions which are not decolorised by mineral acids and are not precipitated by tannin. When their solutions, acidified with sulphuric acid, are shaken with ether, the latter dissolves the colouring matter and leaves a residue when evaporated. They do not dye wool and silk in a neutral bath but do so in an acid bath (with sulphuric acid) ; they are little suitable for cotton.

Acid colouring matters are mostly salts of coloured acids, sulphonic derivatives being especially numerous among them.

Direct or *substantive* colouring matters dye vegetable and animal fibres directly in a bath with a little soap, soda or alkaline salt, without need of a mordant. The benzidine colouring matters, for instance, belong to this group.

Mordant colouring matters dye wool or cotton in neither a neutral, nor an acid, nor an alkaline bath, but act only in presence of a metallic mordant.

Vat colouring matters are insoluble in water and are fixed on the fibre by first reducing them into their water-soluble leuco-derivatives and then re-oxidising these on the fibre in the air ; indigo, the indigoids and indanthrene belong to this class.

Sulphur colouring matters are more or less soluble in water, but readily soluble in alkalies or alkaline sulphides ; when treated with hydrochloric acid or, better, with hydrochloric acid and stannous chloride, they emit hydrogen sulphide ; when burnt they give an odour of sulphur dioxide and leave a more or less abundant residue containing alkaline sulphates and sulphites.

Developed colouring matters are produced directly on the fibre by oxidation (e.g., aniline black) or by diazotisation and coupling (e.g., primuline,

diamine black). They are hence sold not as such but as the products which serve to produce them on the fibre.

Artificial organic colouring matters may be in powder, crystals, lumps or more or less aqueous paste. They exhibit various tints often different from those they impart to the fibre ; they frequently show iridescence and metallic lustre, especially if crystallised.

Most of these colours are soluble in water and in alcohol, some only in alcohol ; less frequently they dissolve in other organic solvents, and some are insoluble even in water and in alcohol. When heated in the air they burn easily with a special odour.

They may be mixed with various extraneous substances, either inorganic or organic, and sometimes in very large amount ; these may be introduced during the manufacture, or may be added either to adjust or attenuate the colour, or as thickening, or to facilitate application and fixation, or as adulterants.

Analysis of an artificial organic colouring matter may be required for various purposes : (1) to determine its nature ; (2) to ascertain the purity and any adulteration ; (3) to determine its value as regards tintorial properties.

The investigations and tests to be made in each case are dealt with in the following paragraphs.

1. Identification of Colouring Matters

Observation of the characters already mentioned for the different classes of colours gives a first indication of the nature of a colouring matter. A systematic investigation may be carried out by various methods, especially that of Green (based on Weingärtner's old method) and that of Rota, modified by Buzzi.

Such systematic methods, described below in their general outlines, allow the nature of a dyestuff to be orientated and the group to which it belongs determined ; its precise definition is not, however, easy in all cases, especially since new colouring matters are continually being put on the market. For such identification, use must be made of the reactions and tests to be found in special textbooks.[1]

Prior to the systematic investigation, certain preliminary tests are necessary to determine if the colouring matter is a single individual or a mixture of several (in the latter case, identification is even more difficult). Such preliminary tests are principally the following :

(*a*) A little of the finely powdered substance is thrown on to a filter-paper, previously wetted with water or alcohol : with a mixture, spots of different colours are formed.

(*b*) A small quantity of the powdered material is allowed to fall on to the surface of concentrated sulphuric acid in a flat porcelain dish : with a mixture, the granules from rings of various colours in the acid.

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[1] G. Schultz : *Farbstofftabellen* (5th edition, Berlin, 1914). See also Allen : *Commercial Organic Analysis*, Vol. V ; Lunge : *Technical Methods of Chemical Analysis*, Vol. II, Part II (London, 1911).

(c) Strips of absorbent paper are hung so that their lower extremities dip into a dilute solution of the colouring matter : if the latter is a mixture, zones of different colours appear on the paper after a time.

(d) Successive quantities of well defatted white woollen yarn are dyed with a solution of the colouring matter until the latter is exhausted : in the case of a mixture the different yarns are differently coloured.

I. Green's Method.[1]—The *reagents* required for differentiation into groups are :

1. A solution containing 5% of tannin and 5% of sodium acetate.

2. Zinc dust.

3. Dilute acetic acid (5%).

4. Dilute ammonia, both aqueous (1 part of concentrated ammonia in 100 parts of water) and aqueous-alcoholic (1 part of concentrated ammonia in 50 parts of water and 50 parts of alcohol).

5. Dilute hydrochloric acid (5 parts of the concentrated acid in 100 parts of water).

6. A solution containing 1 part of potassium permanganate and 2 parts of sulphuric acid per 1000.

7. A solution containing 100 grams of stannous chloride in 100 c.c. of concentrated hydrochloric acid and 50 c.c. of water.

8. A 5% lead acetate solution.

9. 5% and 1% caustic soda solutions.

10. Solid sodium hydrosulphite.

11. A solution containing 10% of chromium fluoride and 5% of sodium acetate.

12. Dilute formic acid (1%).

13. 95% alcohol and ordinary ether.

A test is first made to ascertain if the colours are soluble or insoluble in water; the solubility should be complete, or almost so, in boiling water.

In the case of *colouring matters soluble in water*, a solution (about 1%) is treated with a little of the tannin solution 1. Formation of a precipitate indicates a *basic* or *basic mordant colouring matter* (Group A). If the tannin solution gives no precipitate, a test is made to ascertain if the colouring matter dyes cotton directly without a mordant; to this end a solution of the colouring matter (of the above concentration) is boiled for half a minute in a test-tube with a piece of mercerised white cotton fabric about 2 cm. square, the material being then removed and boiled for a minute with dilute ammonia (1 : 100). If the cotton remains coloured, the substance is a *substantive* or *soluble sulphur colouring matter* (Group B) ; if the cotton is not coloured (or very feebly coloured) the substance is an *acid* or *acid mordant colouring matter* (Group C).

In the case of *colouring matters insoluble in water* (Group D), these may be of the *mordant, developed, sulphur* or *vat* types.

The procedure for these four groups is as follows.

[1] Published some years ago (*Journ. Soc. chem. Industry*, 1893, p. 3) and recently modified and completed by the author with the help of A. E. Woodhead ; *see* A. G. Green : *The Analysis of Dyestuffs* (London, 1915), pp. 41 *et seq.*, and Plates IV-VII.

(*A*) Basic and Basic Mordant Colouring Matters. The hot solution (about 1%) of the colouring matter is treated with a little zinc dust, a few drops of dilute acetic acid being added and the liquid shaken. If the solution becomes decolorised, as is the more commonly the case, a few drops of it are then poured on to a filter-paper, note being made : (1) if the colour reappears in the air in 1–2 minutes, (2) if it does not reappear in the air or does so only very slowly but reappears when the paper is moistened with a drop of the acid permanganate solution (6), or (3) if the colour entirely fails to reappear. If the colour is unaltered by zinc and acetic acid, the reduction is repeated with zinc and dilute hydrochloric acid in the hot.

From the results of these and other subsequent tests—in some cases that with chromium fluoride solution (11)—the nature of the colouring matter is decided in accordance with Table XLIV on p. 427.

(*B*) Substantive and Soluble Sulphur Colouring Matters. A small quantity of the colouring matter is gradually heated to incipient boiling with the stannous chloride solution (7) in a test-tube, the mouth of which is closed with a piece of filter-paper moistened with a drop of lead acetate solution : the formation on the paper of a brown iridescent spot indicates a soluble sulphur colouring matter. The absence of such a spot indicates a substantive colouring matter; the test of reduction with zinc dust and acetic acid and subsequent reoxidation in the air is then made and the results interpreted according to Table XLV on p. 428.

(*C*) Acid and Acid Mordant Colouring Matters. The solution of the colouring matter is treated with zinc dust and acetic acid as described above. In case decolorisation occurs, the original colour may reappear either spontaneously in the air, or only on addition of acid permanganate, or not at all; in the last case, a dyeing test is made with mordanted and non-mordanted wool. For this purpose, pieces of white woollen fabric (defatted) about 2 cm. square and similar pieces mordanted (by boiling for an hour in a solution containing 3% of potassium bichromate—calculated on the weight of the wool) are immersed in a solution of the dyestuff containing one or two drops of the dilute formic acid (12). The solution is heated to boiling and then kept in a boiling water-bath for a quarter of an hour, the fabric being afterwards washed and boiled with the dilute ammonia solution (4) (aqueous-alcoholic in the case of black colours). If the ammonia removes the colour from both fabrics, the substance is an acid colouring matter, whereas, if the mordanted fabric remains coloured, it is an acid mordant colouring matter.

The results of these and subsequent tests indicate the nature of the colouring matter (*see* Table XLVI, pp. 430–1).

(*D*) Colouring Matters Insoluble in Water. A small quantity of the colouring matter is heated with 5% caustic soda solution.

If it dissolves, the alkaline solution is boiled with a little zinc dust and ammonia, the liquid becoming decolorised or changing towards brownish-yellow or brown, and the original colour either reappearing or not in the air. For further subdivision use is made of the stannous chloride test already described.

TABLE XLIV

(A) Basic and Basic-mordant Dyestuffs

Reduce with zinc-dust and acetic acid.

No.	Section	Colour	Dyestuffs
	The solution is decolorised, and the colour returns on exposure to air. The colour of the aqueous solution is:		
1	Red: *Azine Class.*		Induline scarlet, safranine, brilliant safranine, rosolane, neutral red, rhoduline red, brilliant rhoduline red.
2	Orange and yellow: *Acridine Class.*		Acridine yellow, acridine orange, phosphine, rheonine, patent phosphine, diamond phosphine, flavophosphine, coriphosphine, homophosphine, brilliant phosphine, auramine, rhoduline orange, benzoflavine, coriflavine, aurophosphine.
3	Green: *Thiazine Class.*		Methylene green, azine green.
4	**Blue: *Oxazine or Thiazine.*** On the addition of chromium fluoride reagent to a solution of the dyestuff. — Colour precipitated: *Basic-mordant Dyestuff.*		Celestine blue, coreine 2R, ultra cyanine, modern cyanine, phenocyanine, chromocyanine.
5	No precipitate: *Basic Dyestuff.*		Methylene blue, new methylene blue, thionine blue, Capri blue, cresyl blue, brilliant cresyl blue, Nile blue, Basle blue, Meldola's blue, fast navy blue, new blue, metamine blue, naphthol blue, metaphenylene blue, paraphenylene blue, indamine blue, metazine, neutral blue, muscarine, diphene blue, rhoduline blue, rhoduline sky blue.
6	**Violet: *Oxazine or Azine.*** On the addition of chromium fluoride reagent to a solution of the dyestuff. — Colour precipitated: *Basic-mordant Dyestuff.*		Ultra violet, modern violet, modern heliotrope, prune.
7	No precipitate: *Basic Dyestuff.*		Paraphenylene violet, rhoduline violet, rhoduline heliotrope, methylene violet, methylene heliotrope, tannin heliotrope, iris violet, amethyst violet, cresyl fast violet.
8	The solution is decolorised and a pink colour returns on exposure to air: *Safranine Azo Class.*		Indone blue, naphthindone, Janus blue, Janus dark blue, Janus green, Janus black, Janus grey, diazine blue, diazine green, diazine black, diazine brown, brilliant diazine blue, indoine blue, indole blue.
	The solution is decolorised, and the colour returns on spotting with acid permanganate: *Triphenylmethane and Pyrone Classes.* The colour of the aqueous solution is:		
9		Red.	Pyronines, acridine red, rhodamines, rhodines, irisamine, magenta, new fuchsine, isorubine.
10		Green.	Malachite green, brilliant green, diamond green, fast green, new green, methyl green, ethyl green, iodine green, Victoria green, new Victoria green, chrome green.
11		Blue.	Night blue, Victoria blue, new Victoria blue, brilliant Victoria blue, Victoria pure blue, glacier blue, brilliant glacier blue, setocyanine, setoglaucine, setopaline, turquoise blue, rhoduline blue 5B, 6G, chrome blue.
12		Violet.	Crystal violet, methyl violet, brilliant violet, ethyl purple, benzyl violet, Hofmann's violet, chrome violet.
	The solution is decolorised, and the colour does not return either in air or with acid permanganate: *Azo Class.* The colour of the aqueous solution is:		
13		Red.	Rosole red, rosole scarlet, Janus red, diazine red.
14		Orange and yellow.	Chrysoidine, new phosphine, azo phosphine, tannin orange, Janus yellow.
15		Brown.	Bismarck brown, vesuvine, phenylene brown, Janus brown, tannin brown.
	Colour unaltered: *Thiazols and Ketonimides.* On boiling with zinc-dust and dilute hydrochloric acid:		
16		Solution is slowly decolorised.	Thioflavine T, methylene yellow, rhoduline yellow.
17		Solution is slowly decolorised, and on further boiling becomes blue-violet.	Auramine.

TABLE XLV
(B) Salt and Sulphide Dyestuffs

Apply stannous chloride and lead acetate test.

A deep brown stain is produced : *Sulphide Class.*	Little or no brown stain is produced : *Salt Dyestuff.* Reduce with zinc-dust and acetic acid.							
	Colour reduces very slowly and incompletely : *Thiazol Class.*	Decolorised. Colour returns in air : *Stilbene Class.*	Decolorised. Colour does not return in air : *Azo Class.* The colour of the aqueous solution is:					
			Red.	Yellow, orange, and brown.	Green.	Blue.	Violet.	Black.
1	2	3	4	5	6	7	8	9
Water-soluble sulphide colours of the auranol, cross-dye, eclipse, immedial, katigen, kryogene, pyrogene, pyrol, sulphur, thiogene, thion, thional and thioxine series. Rexoll black.	Primuline, sulphine, thioflavine S, thiazol yellow, Clayton yellow, chloramine yellow, brilliant pure yellow, chlorazol fast yellow, diamine fast yellow B, 2 F, M, chlorophenine, oriol yellow, mimosa yellow, Columbia yellow, nitrophenine, triazol fast yellow, dianil pure yellow, naphthamine pure yellow, oxydiamine yellow, oxydianil yellow.	Direct yellow, naphthamine yellow, Mikado yellow, Mikado golden yellow, Mikado orange, sun yellow, curcumine S, stilbene yellow, diamine fast yellow A, chloramine orange, diphenyl fast yellow, diphenyl chrysoin, diphenyl citronine, polyphenol yellow, diamine orange D, stilbene orange.	Pinks, reds, fast reds, scarlets, fast scarlets, brilliant scarlets, garnets, bordeaux, clarets, corinths, rubines and maroons of the benzo-, benzoform, chloramine, chlorantine, chlorazol, Columbia, Congo, cotton, diamine, dianil, dianol, diazanil, diazo, diphenyl, direct, formal, glycine, hessian, naphthamine, oxamine, oxydiamine, para, paranil, rosanthrene, sultan, titan, toluylene, etc., series. Autochrome red, acetopurpurin, anthracene red, azo purpurin, benzo fast eosin, benzopurpurin, brilliant purpurin, deltapurpurin, diazo geranine, erika, geranine, rosanol, rosazurine, solamine red, rosophenine, trona red.	Yellows, oranges, catechins, browns, dark browns, etc., of the benzo, benzoform, catechu, Chicago, chlorazol, Congo, cotton, cupranil, diamine, dianil, diazo, diphenyl, hessian, naphthamine, oxamine, oxydiamine, para, paranil, pluto, pyramine, renol, toluylene, trisulphon, Zambesi, etc., series. Autochrome orange, brilliant orange, Chrysamine, chrysophenine, cresotine yellow, cutch browns, diamine gold, direct browns, polar yellow R conc., polar orange, polar red.	Greens, dark greens and olives of the azidine, benzo, chloramine, chlorantine, chlorazol, Columbia, diamine, dianil, dianol, diazo, diphenyl, direct, eboli, naphthamine, oxamine, para, paranil, renol, triazol, etc., series.	Blues, sky blues, brilliant blues, pure blues, dark blues, new blues, dark blues, navy blues, indigo blues, blue blacks, cyanines, azurines, etc., of the benzo, benzoform, Chicago, chloramine, chlorantine, chlorazol, Columbia, Congo, Coomassie, cotton, diamine, diamineral, dianil, dianol, diazanil, diazo, diphenyl, direct, eboli, formal, hessian, indigene, naphthamine, naphthogene, oxamine, oxychlorazol, para, polyphenol, renol, solamine, sulphon, toluylene, Zambesi, etc., series. Autochrome blue B, cupramine brilliant blue, diaminogen, diazurine, indazurine, metazurine, naphthazurine, oxydiaminogen, sulphon-cyanines, tolyl blue G R and 5 R.	Violets and heliotropes of the benzo, benzoform, brilliant Congo, chloramine, chlorazol, Columbia, diamine, dianil, dianol, diazo, diphenyl, direct, formal, naphthamine, oxamine, oxydiamine, para, rosanthrene, trisulphon, etc., series. Azo mauve, azo violet, benzo fast heliotrope, chlorantine lilac, hessian purple.	Blacks, fast blacks, jet blacks, deep blacks, greys, etc., of the benzo, chloramine, chlorazol, Columbia, Coomassie, cotton, diamine, diamineral, dianil, dianol, diazanil, diazo, diphenyl, direct, formal, indigene, ingrain, isodiphenyl, naphthamine, oxamine, oxydiamine, para, paradiamine, paranil, pluto, plutoform, renol, titan, toluylene, Zambesi, etc., series. Diamine neron, melantherin.

If the colouring matter is insoluble in caustic soda, its solubility in boiling 95% alcohol is tested. For further subdivision, use is made, for colouring matters soluble in alcohol, of the test with zinc dust and acetic acid, and for those insoluble in alcohol, of the tests with stannous chloride and with sodium hydrosulphite. The latter test is carried out by heating a little of the substance for 5–10 minutes at about 80° with about an equal amount of solid sodium hydrosulphite and a little 1% caustic soda solution ; the substance is dissolved and reduced to the leuco-derivative, the colour of this being observed.

A résumé of the procedure is given in Table XLVII on p. 432.

II. Buzzi's Modification of Rota's Method.[1]—For the first separation into groups, based on the reducing action of stannous chloride in presence of hydrochloric acid and subsequent reoxidation, the following *reagents* are required:

1. Stannous chloride solution obtained by dissolving tin in hydrochloric acid and then diluting with 3 parts of water.

2. 10% sodium hydroxide solution.

3. 10% ferric chloride solution.

To ascertain if the colouring matter is reduced by stannous chloride, about 5 c.c. of its dilute (about 1 : 10000) aqueous or aqueous-alcoholic solution are treated with 5–10 drops of concentrated hydrochloric acid and then as much of the stannous chloride solution, the liquid being heated with shaking to incipient boiling.

If the decolorisation occurs, the reduced liquid is divided into two portions, it being noted if the colour reappears (1) on shaking in the air after neutralisation with sodium hydroxide, or (2) on treatment with ferric chloride. Non-reappearance of the colour indicates *reducible and non-reoxidisable colouring matters* (Group A) and reappearance of the colour, *colouring matters reducible to leuco-derivatives and reoxidisable* (Group B).

If decolorisation is not brought about by stannous chloride, the colouring matter is non-reducible (*carboquinone colouring matters*). In such case a little of the colouring matter is treated with caustic soda in slight excess, heating if necessary: more or less decolorisation or precipitation of the solution indicates *amino-colouring matters* (Group C), whereas increase of the colour and solubility indicates *phenolic colouring matters* (Group D).

With each of these four groups the procedure is as described later. In the first place, however, the colouring matter is investigated with reference to its tintorial properties by means of dyeing tests on non-mordanted cotton or wool, on wool mordanted with aluminium sulphate and cream of tartar, on wool mordanted with chromium fluoride and cream of tartar, on cotton mordanted with tannin and then with tartar emetic, on cotton mordanted with aluminium acetate and on cotton mordanted with chromium acetate.

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[1] G. Rota : New method of analysis of artificial colouring matters derived from tar, *L'Industria*, 1891, p. 698, and *Rivista d'igiene e sanità publica*, 1893, IV, p. 789. Buzzi: private communication and *Atti del 2° Congresso naz. di Chim. appl. in Torino* (1911), p. 515. See also report by F. Reverdin to the International Committee on Analysis (Sub-committee XI) of the International Congress of Applied Chemistry at New York (1912).

TABLE

(C) Acid and Acid-

Reduce with zinc-dust

Colour unaltered: *Quinoline Class.*	Decolorised. Colour returns in air: *Azines, Thiazines,* and *Pyrones.*	Decolorised. Colour returns on spotting with acid permanganate: *Triphenylmethane* and *Pyrone Classes.* Acidify the aqueous solution, and shake with ether.		Decolorised. Colour does not return either in air or with acid permanganate: unchromed wool in the dye solution with a few drops of formic acid. Colour stripped from both patterns: *Acid Dyestuff.* Colour of solution is:					
		Ether layer is coloured.	Ether layer is colourless.	Red.	Yellow, Orange, or Brown.	Gre n.	Blue.	Violet.	Black.
1	2	3	4	5	6	7	8	9	10
Quinoline yellow, quinaldine yellow.	Fast acid violet, fast acid red A, fast acid blue R conc., violamine, induline W.S., fast blue, solid blue, nigrosine W.S., silver grey, rosinduline, azo carmine, naphthyl blue, indochromine, brilliant alizarine blue, thiocarmine, alizarine green B, C, delphine blue, brilliant delphine blue, lanoglaucine, chromazurine, lazuline blue, acid cyanine, wool fast blue, wool fast violet, indigo carmine.	Fluoresceine, uranine, eosine, phloxine, erythrosine, rose bengale, methyl eosine, eosine scarlet, cyanosine, metachrome violet.	Fast acid eosine, fast acid phloxine, fast acid magenta, acid rosamine, acid rhodamine, sulpho rosazeine, xylene red, brilliant kitone red, chromorhodine, acid magenta, acid violets, alkali violets, formyl violet, Guinea violet, kitone violet, fast acid violet 10 B, patent blues, erioglaucine, eriocyanine, neptune blue, xylene blue, kitone blue, brilliant acid blue, cyanole, cyanine, alkali blues, water blues, methyl blues, wool blue, brilliant milling blue, isamine blue, brilliant dianil blue, brilliant chlorazol blue, acid greens, Guinea green, neptune green, brilliant milling green, erioviridine, light green, wool green, agalma green, naphthalene green, cyanol green, alkali fast green.	Acetyl red, amaranth, amido naphthol red, anthosine, azo acid carmine, azo acid red, azo coccine, azo eosine, azo fuchsine, azo milling red, azo rubine, Biebrich acid red,;Biebrich scarlet, Bordeaux, brilliant acid carmine, brilliant cochineal, brilliant croceine, eriorubine, fast red, Guinea red, lanafuchsine, naphthol red, palatine scarlet, ponceau, sorbine red, supramine red, Victoria scarlets, wool reds, wool scarlets, lithol reds, lake reds.	Martius yellow, naphthalene yellow, acid yellow, citronine, naphthol yellow, tartrazine, tartraphenine, xylene yellow, Guinea fast yellow, fast light yellow, kitone yellow, fast acid yellow, Indian yellow, supramine yellow, sulphon yellow, fast yellow, azo flavine, brilliant yellow, palatine light yellow, azo acid yellow, normal yellow, phenoflavine, Victoria yellow, metanil yellow, orange II, IV, etc., fast light orange, wool fast orange, sulphon orange, brilliant orange, croceine orange, acid brown, fast brown, sulphon acid brown, resorcine brown, supramine brown, Guinea brown, neptune brown, wool brown.	Sulphon acid green, naphthol green B.	Azo acid blue, azo cyanine, azo merino blue, azo navy blue, brilliant cloth blue, chromazone blue, domingo blue black, erio fast brilliant blue, ethyl acid blue, cresol blue black, lanacyl blue, naphthol blue black, naphthylamine blue black, orthocyanine, phenyl blue black, sulphon acid blue, tolyl blue S B, S R, S T.	Azo acid violet, anthosine violet, domingo violet, erio fast purple, ethyl acid violet, fast sulphon violet, indo violet, lanacyl violet, omega light claret, omega light violet, sulphon violet, Victoria violet, wool violet.	Acid black, agalma black, alphanol black, amido acid black, amido naphthol black, amido black, anthracite black, azo acid black, azo merino black, Biebrich patent;black, brilliant black, Coomassie wool black, ethyl black, fast sulphon black, Guinea black, kresol black, naphthalene acid black, naphthol black, naphthylamine black, nerol, ortho black, palatine black, phenol black, phenylamine black, sulphon acid black, sulphocyanine black, supramine black, tolyl black, Victoria black, wool black.

XLVI

mordant Dyestuffs

and acetic acid.

Azo Class (also Nitro and Nitroso). Boil small pieces of chromed and (1:100). Wash thoroughly and boil with ammonia (1:100).						Not decolorised, but changed in shade: Anthracene Class. The colour of the reduced solution is:		
Little or no colour is stripped from the chromed pattern: *Acid-mordant Dyestuff*. Colour of solution is:							Bright yellow, orange, or orange-brown.	
Red.	Yellow, orange, or brown.	Green.	Blue.	Violet.	Black.	Red.	On the addition of a few drops of dilute caustic soda (1:20), no change occurs.	On the addition of a few drops of dilute caustic soda (1:20), the colour becomes more intense, and bluer
11	12	13	14	15	16[1]	17	18	19
Acid chrome red, acid anthracene red, acid alizarine red, anthracene chrome red, acid alizarine garnet, azo alizarine carmoisine, chrome fast Bordeaux, chrome fast garnet, chromotropes, diamond red, eriochrome red, eriochrome Bordeaux, omega chrome red, oxychrome garnet, palatine chrome red, eriochrome olive, palatine chrome violet, anthracene chrome violet, acid chrome blue, azo chrome blue, chrome fast blue, chromotrope blue, omega chrome blue.	Acid alizarine brown, acid anthracene brown, alizadine brown, anthracene acid brown, anthracene chrome brown, chromal brown, chrome fast brown, chromoxane brown, eriochrome brown, monochrome brown, oxychrome brown, palatine chrome brown, salicine chrome brown, salicine red brown, acid chrome yellow, alizadine orange, alizarine yellows, anthracene orange, anthracene yellow, azo alizarine orange, azo alizarine yellow, chrome fast yellow, chromocitronine, chrome yellow, chrome orange, diamond orange, eriochrome yellow, eriochrome phosphine, metachrome yellow, mordant yellow, salicine orange.	Chrome green G.	Chrome cyanine, chrome fast cyanine, metachrome blue, palatine chrome blue.	Acid alizarine green 2 B, acid chrome green, chrome fast green, diamond green, eriochrome green, fast chrome green P, omega chrome green, cyprus green, oxychrome violet, eriochrome violet, acid alizarine violet, chrome fast violet, monochrome blue, oxychrome blue, salicine chrome blue, salicine indigo blue.	Acid alizarine black, acid chrome black, anthracene acid black, anthracene chrome black, chromate black, chrome acid black, chrome fast black, diamond black, eriochrome black, fast chrome black, fast mordant black, monochrome black, omega chrome black, oxychrome black, palatine chrome black, salicine black.	Alizarine cyanol E F, alizarine saphirol, alizarine direct cyanine, alizarine direct blue E B, E 3 B, anthraquinone blue, anthracyanine, eriocyanine L M, fast sky blue, brilliant anthrazurol, alizarine emeraldol G, acid alizarine green G.	Alizarine direct blue B, alizarine cyanol B, alizarine astrol, alizarine uranol, alizarine sky blue, alizarine carmine blue, cyananthrol, alizarine irisol, alizarine cyanol violet, alizarine direct violet, anthraquinone violet, alizarine geranol, alizarine rubinol, alizarine cyanine green, alizarine brilliant green, alizarine direct green, alizarine viridine, brilliant alizarine viridine, anthraquinone green, anthraquinone blue green, monochrome green.	Alizarine red (S marks), Erweco alizarine acid red, alizarine orange S W, alizarine cyanine, brilliant alizarine cyanine, anthracene blue (S Marks), acid alizarine blue, alizarine dark green W, alizarine blue (S Marks), alizarine green S, alizarine black S, alizarine indigo blue (S Marks), cœruleïne (S Marks).

TABLE XLVII

(D) Dyestuffs insoluble in Water : Sulphide, Mordant, Pigment, Spirit Soluble, and Vat Dyestuffs.

Add a small quantity of the dyestuff to 5 per cent. caustic soda, and warm.

The dyestuff dissolves. Add a little zinc-dust and ammonia to the alkaline solution, and boil.			The dyestuff is insoluble in caustic soda. Boil with 95 per cent. alcohol.					
Solution is decolorised, or changed in shade to yellow-brown or brown. On pouring on to filter-paper, original colour returns. Apply stannous chloride and lead acetate test.		Solution is decolorised. On pouring on to filter-paper, original colour does not return : *Mordant Dyes* of the *Nitroso* and *Azo Classes.*	The dyestuff dissolves in 95 per cent. alcohol. Reduce the alcoholic solution with zinc-dust and acetic acid.			The dyestuff is insoluble in 95 per cent. alcohol. Apply stannous chloride and lead acetate test.		
A brown stain is produced : *Sulphide Class.*	No stain is produced : *Mordant Dyes* of the *Anthracene, Pyrone,* and *Oxazine Classes.*		Colour remains unchanged : *Quinoline Class.*	Decolorised, but colour returns in air or on spotting with acid permanganate : *Azine* and *Triphenylmethane Classes.*	Permanently decolorised : *Nitro* and *Azo Classes.*	A brown stain is produced : *Sulphur Vat Colours.*	No brown stain is produced. Reduce with caustic soda (1 per cent.) and hydrosulphite. The dyestuff dissolves : *Vat Dyestuff.*	
							The leuco compound is yellow or clear orange : *Indigoid Class.*	The leuco compound is dark coloured : *Anthracene* and *Naphthacene Classes.*
1	2	3	4	5	6	7	8	9
Insoluble sulphide colours of the auranol, cross-dye, eclipse, immedial, katigen, kryogene, pyrogene, pyrol, sulphur, thiogene, thion, thional, thionol, and thioxine series.	Alizarine, anthrapurpurine, flavopurpurine, purpurine, resoflavine, galloflavine, alizarine black, alizarine brown, anthracene brown, anthragallol, alizarine garnet, alizarine maroon, alizarine blue, anthracene blue, alizarine cyanine, alizarine bordeaux, brilliant alizarine bordeaux, alizarine cyanine black, gallamine blue, gallocyanine, alizarine green, coeruleine, galleine.	Alizarine yellow 2 G, R, anthracene yellow 2 G, Russian green, gambine, fast printing green, Alsace green, resorcin green, dioxine, fast green O, viridone F F.	Quinoline yellow (spirit sol.).	Nigrosine (spirit sol.), induline (spirit sol.), melasine, oil black, spirit black, spirit blue, oleate green.	Sudans, butter yellow, cerasine orange, oil yellow, oil orange, tuscaline orange, pigment chlorin, lithol fast yellow, pigment chrome yellow, cerasine red, lithol fast orange, lithol fast scarlet, autol reds, helio fast red, hansa yellow, lake reds, sitara fast red, pigment orange, pigment red, pigment claret, permanent reds, pigment purple, oil scarlet, oil red, oil vermilion.	Hydron blue, hydron brown, hydron dark blue, hydron olive, hydron violet, cibanone black, cibanone blue, cibanone brown, cibanone green, cibanone olive, indanthrene olive, algol brown B, algol olive, algol dark green, leucol brown, leucol dark green, helindone black, helindone orange D, helindone blue 3 R, indocarbon black.	Vat colours of the ciba, helindone, and thioindigo series. Indigo, bromindigo, brilliant indigos, alizarine indigo, alizarine indigo red, alizarine indigo grey, algol scarlet, thioindone green, vat red.	Vat colours of the Algol and indanthrene series. Cibanone orange, anthraflavone, helindone fast scarlet C, helindone orange G R N, helindone black G, 2 R G, helindone yellow A N, helindone brown A N, C R, ciba indigo yellow 3 G, ciba yellow G, 2 R, 5 R, ciba red R, ciba scarlet G, ciba brown R, leucol brown B, leucol dark green B, leucol yellow G, thioindigo scarlet 2 G, Sirius yellow, helio fast yellows, helio fast pink.

From the results of such tests conclusions are drawn in accordance with the following scheme :

Cotton and wool, even non-mordanted, are dyed in a dye bath containing sodium sulphate ; dyed natural wool gives up its colour in a slightly alkaline medium to white cotton . . .   *Substantive colouring matters*

Non-mordanted cotton is dyed little or not at all in a bath of the colouring matter containing sodium sulphate, even when acidified with acetic acid

Natural and mordanted wools are equally dyed in a bath containing sodium sulphate and acidified with acetic acid

Cotton mordanted with aluminium or chromium is not dyed, but that mordanted with tannin is strongly dyed in the above bath ; dyed natural wool gives up its colour to tannin-mordanted cotton in a slightly alkaline medium . . . .   *Basic colouring matters*

Mordanted cotton is dyed little or not at all ; dyed natural wool does not give up its colour to white cotton in a slightly alkaline medium, and on acidification takes up again the colour given to the alkaline medium . . . .   *Acid colouring matters*

Natural wool is dyed in the above bath, but the colour is only slightly resistant to soap ; mordanted wool is dyed more intensely and gives faster colours ; the colour varies with the mordant

Mordanted cotton is dyed with feeble intensity . . . .   *Acid phenolic colouring matters*

Tannin-mordanted cotton is dyed little or not at all, whereas aluminium- or chromium-mordanted cotton is deeply coloured . . .   *True phenolic colouring matters*

The procedure to be followed in each of the four groups *A*, *B*, *C* and *D* is described briefly below.

(*A*) Reducible and Non-reoxidisable Colouring Matters. To this group belong nitro-, nitroso-, azo-, azoxy- and hydrazo-colouring matters, which are distinguished as indicated in Table XLVIII.

<div align="center">Table XLVIII</div>

(*A*) Reducible and Non-reoxidisable Dyestuffs

The solution of the colouring matter is coloured orange with alkali; the colouring matter deflagrates when heated; wool is dyed in an acid bath: *Nitro-colouring matters.*			The alcoholic solution gives a blue coloration with phenol and conc. H_2SO_4 (Liebermann's reagent); with ferrous sulphate a green lake: *Nitroso-colouring matters*	The solution does not give the reactions indicated, for the two preceding subdivisions: *Azo- azoxy-* and *hydrazo-colouring matters.*				
Ether extracts the colour from the alkaline solution: *Nitramines.*	Ether does not extract the colour from the alkaline solution: *Nitrophenols.*			*Basic.*	*Acid.*	*Acid phenolic.*	*Phenolic.*	*Substantive.*
	Ether extracts the colour from the acid solution: *Non-sulphonated.*	Ether does not extract the colour from the acid solution: *Sulphonated.*						
1	2	3	4	5	6	7	8	9
Auranzia.	Picric acid, Victoria yellow, Martius yellow.	Naphthol yellow S.	Naphthol green B, dioxine, gambine.	Bismarck brown, chrysoidin, etc.	Azoflavine, croceine orange, ponceaux, scarlets, archil substitutes, roccellin, azo acid violet, etc. ; tartrazine.	Diamcnd yellow, cloth yellow, chromotropes, etc.	Diamond flavine G, alizarine yellows G G W and R W, etc.	Benzo, diamine, Congo, Colombia, direct, oxamine, oxydiamine dyestuffs, etc. ; Mikado yellow and orange, curcumine.

(*B*) REDUCIBLE AND REOXIDISABLE COLOURING MATTERS. In this group are the quinoniminic colouring matters and also indigo carmine. The further treatment is as indicated in Table XLIX.

TABLE XLIX

(*B*) **Reducible and Reoxidisable Dyestuffs**

Reduction with stannous chloride and hydrochloric acid proceeds easily in the cold.			Reduction with stannous chloride and hydrochloric acid takes place with difficulty and only in the hot : *Azines.*	
The colouring matter does not contain sulphur and is of basic or phenolic character : *Indamines, indophenols, oxazines.*	The colouring matter contains sulphur (not sulphonic) and is basic, acid phenolic or acid : *Thiazines.*	The colouring matter is sulphonated.	*Basic.*	*Acid.*
1	2	3	4	5
New methylene blue G G, Nile, new and Capri blues ; gallocyanine, phenocyanine, etc.	Methylene blue, new methylene blue N, brilliant alizarine blue ; thiocarmine, etc.	Indigo carmine.	Safranine, tannin heliotrope, Magdala red, azine green ; induline (spirit soluble), nigrosine (spirit soluble), etc.	Rosinduline, azocarmine, induline (water soluble), nigrosine (water soluble), etc.

(*C*) Non-reducible, Aminic (Aminocarboquinonic) Colouring Matters. In this group are the amino-derivatives of di- and tri-phenylmethanes, with the acridine, quinoline and thiazole colouring matters, which are distinguished as indicated in Table L.

Table L

(*C*) **Non-reducible Aminic Dyestuffs**

Ether extracts the colouring matter from its slightly alkaline aqueous or aqueous-alcoholic solution ; the ethereal layer when shaken with acetic acid, turns :				Ether does not extract the colouring matter from its alkaline solution (the ethereal layer gives no coloration when shaken with acetic acid).	
Yellow or orange with fluorescence : *Acridine colouring matters.*	Yellow, without fluorescence : *Auramine.*	Red, with fluorescence : *Pyronines, rhodamines.*	Red, violet, green or blue, without fluorescence : *Triphenylmethane colouring matters.*	The colour is fixed by wool in an acid bath (acid colouring matter) : *Sulphonated triphenylmethane colouring matters.*	The colouring is fixed directly on cotton (substantive colouring matter) *Thiazole colouring matters.*
1	2	3	4	5	6
Acridine yellow and orange, benzoflavine, phosphine, etc.	Auramine.	Pyronine, rhodamines, rhodines.	Fuchsine ; methyl, ethyl and regina violets ; aniline and Victoria blues ; malachite, methyl, brilliant and Victoria greens, etc.	Acid fuchsine, acid violet ; acid green, guinea green ; alkali blue, marine blue, etc.	Thioflavine, polychromine.

(*D*) Non-reducible, Phenolic (Hydroxycarboquinonic) Colouring Matters. To this group belong the phthaleins, the hydroxylic derivatives of triphenylmethane, the hydroxyketonic colouring matters, also many vegetable colouring matters (e.g., those of yellow wood, quercitron, fustic, Persian berries, woad, etc.). As regards the artificial colouring matters, the group may be subdivided as indicated in Table LI.

TABLE LI

(*D*) **Non-reducible Phenolic Dyestuffs**

The aqueous-alcoholic solution of the colouring matter is treated with a few drops of very dilute (1 : 1000) ferric chloride solution.			
The solution remains unaltered or almost so.		The solution changes to olive green or violet : *Hydroxyketonic colouring matters.*	
The colouring matter is not fixed stably on wool; the alcoholic solution, even when made alkaline, is not fluorescent : *Triphenylmethane colouring matters.*	The colouring matter dyes wool in an acid bath; the alcoholic or alkaline solution is usually fluorescent : *Phthaleins.*	The substance gives a yellow solution with dilute caustic potash : *Monoketonic colouring matters.*	The substance gives a red, violet, blue or green solution with dilute caustic potash : *Quinonic colouring matters.*
1	2	3	4
Aurine, coralline.	Eosine, erythrosines, phloxine, Bengal red.	Alizarine yellow A ; various natural dyestuffs.	Alizarine, alizarine and anthracene dyestuffs.

2. Detection of Extraneous Substances in Colouring Matters

Of the extraneous substances which may be found n artificial organic colouring matters (besides water, especially in pasty materials), some may be derived from the manufacture, such as sodium chloride and sulphate; others, such as zinc and ferric chlorides, may form integral parts of certain colours, which are prepared as double salts with these chlorides; others may consist of mordants mixed with the colouring matter, such as aluminium, iron, chromium, antimony and copper salts, cream of tartar, tannin, etc.

Various substances, such as sodium carbonate (especially with eosin), magnesium sulphate, dextrin, starch, glucose or sugar may be added as thickening or to adjust the tint, and others, such as fatty substances, fatty acids, paraffin wax or ceresine (in colours for fats and waxes), to facilitate the use for particular purposes.

Lastly, some of the substances already mentioned may be added as adulterants, and for the same purpose use may be made of such materials as potassium oxalate and oxalic acid (found in fuchsine), and bronze powders (in colouring matters with metallic lustre). Arsenic may occur as impurity in certain aniline colouring matters, especially in certain fuchsines.

The detection and determination of the principal extraneous substances mentioned above are carried out as follows.

1. Water.—This is determined in pasty colours by drying a known weight of the substance at 100° to constant weight.

2. Sodium Chloride.—A direct test with silver nitrate in a solution of the colouring matter acidified with nitric acid cannot be made in all cases, since many basic colouring matters are in the form of hydrochlorides. In such cases the colouring matter is carefully burnt or completely carbonised, the residue taken up in water, the solution filtered and the filtrate tested for sodium chloride in the usual way.

Some colouring matters containing chlorine, such as eosin, may leave ash containing haloid salts. In this case the solution of the colouring matter, acidified with sulphuric acid, may be extracted with ether and the aqueous liquid tested for chlorine and sodium.

When the colouring matter is soluble in alcohol, it is treated with this solvent and the insoluble residue tested for the salt.

To determine the sodium chloride quantitatively, the same methods may be used, a weighed quantity of the material being taken and the chlorine in the ash or the acid liquid extracted with ether determined in the usual way: $Cl \times 1 \cdot 6486 = NaCl$.

3. Sodium Sulphate.—The presence of this salt in the ash does not always indicate its addition to the colouring matter, since sulphonic compounds leave a large amount of ash containing this salt. Added sodium sulphate is hence tested for as follows:

The solution of the colouring matter, acidified with hydrochloric acid, is treated with barium chloride, which gives a precipitate containing, besides barium sulphate from the sodium sulphate, also the barium salt of the sulphonated colouring matter. The precipitate is filtered off and treated with ammonium carbonate, which converts the sulphonate into barium

carbonate; the insoluble part is washed and then treated with dilute hydrochloric acid, which dissolves the barium carbonate; any residue of barium sulphate will then be due to the presence of sodium sulphate in the colouring matter. The test may be made quantitative: 1 part BaSO = 0·6086 part Na_2SO_4.

With azo-colouring matters the aqueous solution may be treated with pure sodium chloride so as to precipitate the sulphonic colouring matter completely, the filtrate being tested for sodium sulphate in the usual way.

With colouring matters soluble in alcohol, it is sufficient to treat with this solvent, added sodium sulphate then remaining undissolved.

4. Detection of Magnesium Sulphate.—The presence of magnesium in the ash indicates addition of magnesium sulphate to the colouring matter.

5. Detection of Alkaline Carbonates.—A colouring matter containing admixed alkali carbonate effervesces with acid; the carbon dioxide may be determined and the carbonate hence calculated.

6. Dextrin.—The presence of dextrin may be recognised by its peculiar odour, which is observed best if the colouring matter is dissolved in hot water or heated directly in a test-tube.

For the determination, 1–2 grams of the colouring matter are treated with about 95% alcohol and allowed to settle, the liquid being decanted off and the residue dissolved in a very small quantity of water and reprecipitated with alcohol; the liquid is again decanted off and the residue washed with alcohol, dried at 100° and weighed. That this consists of dextrin is confirmed by polarimetric observation of its aqueous solution.

If the colouring matter is insoluble in water, it may be treated with water and the dextrin tested for and determined in the aqueous liquid.

7. Detection of Starch.—The colouring matter is treated in the cold with water or alcohol, the insoluble residue being examined microscopically.

8. Detection of Glucose and Saccharose.—With colouring matters insoluble in water, these may be detected in the aqueous extract. Colours soluble in water and in alcohol may be treated in the cold with absolute alcohol (best mixed with a little ether) and the insoluble residue examined.

Further, an aqueous solution of the colouring matter may be treated with basic lead acetate (a basic colouring matter should first be precipitated with tannin), the excess of lead eliminated, the liquid filtered and the sugars tested for or determined saccharimetrically or with Fehling's solution.

9. Detection of Fats, Fatty Acids, Paraffin Wax and Ceresine.—The substance is treated in the cold with ether, the insoluble residue being filtered off and washed with ether. The ethereal liquid is shaken in a separating funnel with moderately concentrated hydrochloric acid, the aqueous acid layer being separated and the treatment repeated until the ethereal liquid is as far as possible colourless; after being shaken repeatedly with water to remove excess of acid, the ethereal liquid is filtered through a dry filter and the ether then evaporated. The residue obtained is examined by determining the acid and saponification numbers and, if necessary, by separating the unsaponifiable substances and observing their properties.

10. Detection of Arsenic.—This may be effected in Marsh's apparatus (*see* Flesh Foods). To determine the arsenic, an acidified solution of the

colouring matter is treated with bromine water and then excess of ammonia ; the liquid is filtered, if necessary, and magnesia mixture added in the usual way.

11. Heavy Metals.—These are detected in the ash. Iron or zinc may be present naturally, since certain colouring matters are double salts with ferric or zinc chloride (*see* above).

3. Tintorial Value of Colouring Matters

Besides testing for extraneous substances, it is also necessary to know how much actual colouring matter is present and if the requirements as to dyeing value are met.

The necessary data are obtained by tests 1 and 2, which are carried out in comparison with a *standard* colouring matter of the same kind and of the desired purity and value.

1. Colorimetric Test.—Equal weights of the colouring matter under examination and of the standard are dissolved in equal quantities of water or alcohol and the intensities of colour of the two solutions compared by means of a colorimeter.

2. Dyeing Test.—The two colouring matters are then used to dye equal quantities of wool, silk or cotton yarn or fabric, according to the uses for which the colouring matter is intended, the colours obtained being compared.

Dyeing tests give reliable results only when carried out under identical conditions as regards concentration and temperature of the bath, additions made to it, duration of the operation, preliminary (e.g., method of mordanting) and subsequent treatments (washing, drying, etc.).

If the colour obtained is less than that given by the standard, the operation is repeated with the same quantity of the fibre, but with various smaller amounts of the standard colouring matter, so as to obtain a scale of comparison.

Naturally the dyeing procedure varies with the type of colour (basic, acid, mordant, substantive). In order, however, that valid conclusions may be drawn, the procedure should be that used industrially, this being usually indicated in the instructions supplied with the colouring matter.

3. Fastness towards Various Agents.—This is tested by fixing the colour on cotton or wool and testing this as indicated later (*see* Chapter XVI).

Chapter XVI

TEXTILE FIBRES, YARNS, FABRICS

Of the numerous textile fibres known, relatively few are of commercial importance, the principal ones being : cotton, flax, hemp, ramie, jute, wool, silk and artificial silk. These fibres are used to make the different kinds of yarn from which fabrics of various types are woven.

Tests are made on these products to determine their value and to investigate those requisites which render them adapted to their particular uses. These tests may be reduced to three series of observations, namely, microscopic, chemical and physico-mechanical.

1. Microscopic Examination

As with the starches, so also with textile fibres, the microscope furnishes the most certain means for their recognition. As regards the general technique of microscopic practice, reference may be made to the section dealing with flours.

In the case of textile fibres, the most suitable magnification is about 250 diameters. It is, however, convenient first to make an examination under a magnification of 50–60 diameters, so that a greater length of the fibre may be viewed at one time. A low magnification is necessary also when it is desired to find any particular point, such as the ends of the fibres. The plates at the end of this chapter show views of the different fibres taken by means of a drawing apparatus with a magnification of about 140. A collection of fibres of known origin will be found useful, comparison tests being then possible.

1. Instruments and Accessories.—The making of microscopic preparations of the fibres requires, besides ordinary slides and cover-glasses, a number of needles, a penknife, a pair of small forceps and a good magnifying lens or, better, a dissecting microscope. To prepare sections of the fibres a good razor is necessary, a cork or a wooden support being utilisable in place of a microtome, as indicated below.

2. Microchemical Reagents and Reactions.—The principal reagents required are as follows :

(1) IODINE AND SULPHURIC ACID. This consists of :

(*a*) A solution of iodine, obtained by saturating a 1% potassium iodide solution with iodine.

(*b*) A sulphuric acid solution obtained by adding to 2 volumes of pure, concentrated glycerine, firstly, 1 volume of water, and then, gradually and

441

with vigorous cooling, 3 volumes of concentrated sulphuric acid. The concentration of the latter in the reagent is of great importance and it is well to test the reagent, both immediately after making and from time to time afterwards, the tendency of the acid to become diluted rendering necessary the occasional addition of fresh acid or the renewal of the reagent.

A microscopic preparation is made, as described later, of cotton or flax fibres obtained from white fabrics repeatedly washed. These fibres are treated for about 1–2 minutes with the iodine solution, which is then eliminated by careful and complete absorption with thin strips of filter-paper.[1] One or two drops of the acid prepared as above are added, the cover-slip placed and the preparation observed under the microscope. If the concentration of the acid is correct, the flax and cotton fibres are coloured blue without being deformed. If, however, the coloration is feeble and tends to red, the acid is too dilute, while if the fibres swell, it is too concentrated.

By means of this reagent it is easy to distinguish fibres composed of cellulose from those more or less lignified, since the former are coloured blue and the latter yellow.

(2) ZINC CHLORIDE-IODINE. The two following solutions are prepared:

(a) 40 grams of dry zinc chloride in 20 c.c. of water;

(b) 4·2 grams of potassium iodide and 0·2 gram of iodine in 10 c.c. of water.

The two solutions are mixed, left to stand, and the clear liquid decanted off and kept in the dark after addition of a crystal of iodine.

This reagent, applied to natural, dry fibres, colours the cellulose of cotton, flax, hemp, ramie, etc., violet, and that of wood blue, while lignified fibres are dyed yellow.

(3) PHLOROGLUCINOL AND CONCENTRATED HYDROCHLORIC ACID. 1 gram of phloroglucinol is dissolved in 80 c.c. of alcohol. Fibres steeped for a few minutes in this reagent and then treated with concentrated hydrochloric acid, assume a bright reddish-violet coloration if lignified.

(4) OTHER REAGENTS. These are such as are commonly used in ordinary chemical analysis, the principal ones being: 1% caustic potash, 0·1% sodium carbonate, 3% hydrochloric acid, nitric, chromic and sulphuric acids, chlorine water, hydrogen peroxide, Schweitzer's reagent (prepared by treating copper sulphate solution with caustic potash, collecting and washing the precipitate and dissolving it, while still wet, in the least possible quantity of concentrated ammonia), ruthenium red (5–10 mgrms. in 10 grams of water; this should be freshly prepared and kept in the dark), alcohol, etc.

3. Preparation of the Fibres for Microscopic Examination.

(a) RAW VEGETABLE FIBRES. These are often united in bundles and must be first treated with boiling 1% caustic soda or potash in order to separate the individual fibres. The use of acid reagents such as nitric acid and potassium chlorate, or chromic acid, is to be avoided, since these destroy the lignin and rapidly attack the cellulose also.

After treatment with the alkaline solution, the fibres are washed with

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[1] When this reagent is used, great care should be taken that the liquids are not allowed to issue from the cover-glass and damage the front lens of the objective.

water and a small quantity placed on a microscope slide and carefully separated under a lens or dissecting microscope with a couple of needles.

To bring clearly into evidence the characteristic structure of the fibres, these are stained with the iodine-sulphuric acid reagent, which also serves to detect, by the violet-blue or yellow colour assumed by the fibres, if the latter consist of pure cellulose or of more or less lignified cellulose.

(b) INTENSELY COLOURED ANIMAL FIBRES. Some animal fibres are so rich in pigment that microscopic observation is rendered difficult and uncertain. Such are best decolorised by immersing them for at least half an hour in concentrated hydrogen peroxide (100 vols.). Pure nitric acid may also be used, care being taken to watch the decolorisation and restrict it to the lowest limit allowing of the observation being made ; for this purpose the fibres are examined microscopically from time to time during the treatment. As a rule the desired end is attained in 10–15 minutes. The decolorised fibres are carefully washed with water and dried.

(c) YARN. When the yarn is not intensely coloured or dressed, it may be used directly for microscopic examination. Three or four of the fibres are placed on a microscope slide and held firmly with the finger while the blade of a penknife is passed gently over them to remove any flocculent matter. If the fibres appear lignified and hence stiff, they may be soaked in water and glycerine before being scraped. When the fibres are slender and flocculent like cotton, a little of the yarn is placed on a slide together with a drop of water and glycerine or of the reagent to be used and the fibres separated and covered with a cover-slip, inclusion of air-bubbles being avoided.

If the fibres are strongly coloured or dressed, they are cleaned as far as possible by boiling with dilute sodium carbonate solution (0·1%) and then with 3–5% hydrochloric acid in the manner indicated on p. 458 for determining the dressing in cotton fabrics. If the coloration is not sufficiently diminished in this way, the fibres may be treated with chlorine water (not too concentrated) or with dilute chromic or oxalic acid solution. They are then washed well in running water.

For heavily weighted silk, other treatment may also be used (see p. 460).

(d) FABRICS. These are first disintegrated into their elementary fibres. Care should be taken that other fibres sometimes occurring in fabrics for ornament or design do not escape attention. With velvet the pile is examined separately. When the fabric is intensely dyed and dressed, the colouring matter and the dressing are removed by means of the procedure indicated above for yarns.

4. Preparation of Sections of the Fibres.—Identification of animal or vegetable fibres is based mainly on the physical characters, the fibres being mostly so transparent that their form and structure, and particularly the thickness of the walls and the form of the internal canal or lumen, are easily observed. In some cases, however, owing to the close resemblance between certain fibres, recognition is doubtful. This is the case, for instance, with the poorer qualities of flax and hemp, and with certain types of artificial silk. In these instances the transverse sections of the fibres are studied, these permitting of observation of the thickness of the walls, the strata

composing them, the form of the internal cavity and any contents there may be.

These sections are prepared in the following manner :

The fibres are united in a bundle about 3 mm. in diameter and 3–4 cm. in length—the fibres being placed parallel—and wetted with a glue prepared by dissolving 1 part of good gelatine in $1\frac{1}{2}$ parts of water and adding to the hot liquid 1 part of glucose syrup.[1] When the fibres are thoroughly impregnated with the glue, they are pressed between the fingers and stretched so as to glue them all together and to expel excess of glue and air adhering to the fibres, the latter being then left hanging from a wire to dry in the air. When the small cylinder of fibres is sufficiently hard to be cut without bending, it is fixed in a microtome or, more simply, between the two halves of a cork cut lengthwise, these being then bound together with thread.[2] With a good razor sections of the fibres as thin as possible are then cut, care being taken to collect especially small fragments which become detached owing to their extreme thinness. The sections thus obtained, transferred to a slide by means of a brush and then treated with a drop of water to dissolve the glue, are ready for observation. The sections may also be subjected to the microchemical reactions already mentioned for the fibres themselves.

5. Microscopic Measurements.—The measurements sometimes made on microscopic preparations are expressed in thousandths of a millimetre (μ) and are made by means of an eyepiece micrometer. This consists of a glass disc with 1 cm. scratched or photographed on it and divided into 100 parts ; it is fitted on a ring inside a suitable eyepiece which can be unscrewed and opened about half-way down.[3] With this eyepiece the image of the preparation and that of the micrometer scale are observed simultaneously. The makers of the microscope indicate with how many thousandths of a millimetre one division of the micrometer corresponds for each of the different objectives.[4]

The eyepiece is turned so that the image of the micrometer scale covers the object to be measured and the number of divisions occupied read off, the corresponding number of μ being easily calculated.

Since, however, the magnitude of the image varies with the length of the microscope tube, the latter must be made the same as that used when

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[1] This glue may be stored in a wide-necked jar fitted with a cork, a piece of camphor the size of a pea being added to protect it from moulds. In the cold the glue becomes solid, but if warmed somewhat before use it regains its original fluidity.

[2] Use may also be made of a kind of wooden pincers which squeeze the bundle in a convenient cylindrical cavity by means of a screw.

[3] A fairly weak eyepiece, e.g., No. 2, is usually employed.

[4] These values may be easily calculated or verified by means of an objective micrometer, which consists of a glass strip of the dimensions of an ordinary microscope slide with an exact millimetre, divided into 100 equal parts, scratched or photographed in the middle. If this scale is observed like an ordinary slide, the micrometer eyepiece being also used, the number of divisions on the latter corresponding with a certain number on the objective micrometer is found. The value of each division of the eyepiece micrometer in thousandths of a millimetre is then easily calculated. Thus if 80 divisions of the eyepiece micrometer correspond exactly with 24 of the objective micrometer, i.e., with 240 thousandths of a millimetre, each division of the eyepiece micrometer will be equal to 3 thousandths (0·003) of a millimetre.

the value of the eyepiece micrometer is established. In practice a tube-length of 16 cm. is used, this length being marked on the tube.

Measurements are usually made on dry preparations in order to avoid the swelling of the fibres in a liquid. In this case the microscope slide is conveniently smeared with a dilute hot gelatine solution, on which the fibres are placed immediately.

<div align="center">TABLE LII</div>

Microscopic Characters of Vegetable Fibres

Fibre.	Microscopic Appearance		Dimensions.		Coloration with the Iodine-sul-phuric Acid Reagent.
	of the Fibre	of Internal Channel.	Length mm.	Diam. μ.	
Cotton (Gossypium)	Twisted ribbon	Wide, about $\frac{1}{5}$	10–60	12–42 (25)	Blue
Flax (Linum usitatissimum)	Cylindrical; transverse striæ	Narrow	20–50	16–25 (20)	Blue
Hemp (Cannabis sativa)	Crushed cylinder; longitudinal and transverse striæ	Wide, about $\frac{1}{2}$	10–55	10–45 (33)	Greenish-blue
Ramie (Boehmeria nivea)	Wide ribbon, distinct oblique striæ	Wide, about	60–260	48–80 (55)	Blue
Jute (Corchorus) .	Cylindrical, no striæ	Irregular	1–5	10–32 (22)	Yellow, brownish-yellow
New Zealand Flax (Phormium tenax)	Narrow, cylindrical, no striæ	Narrow, about $\frac{1}{6}$	3–10	8–19 (12)	Greenish-yellow
Manila hemp (Musa Texilis)	Cylindrical, no striæ	Marked, about $\frac{2}{5}$	2–3	12–40 (24)	Yellow
Agave, Pita, Sisal hemp	Cylindrical, no striæ	Wide, about $\frac{1}{2}$	1–5	20–32 (26)	Yellow, brownish-yellow
Esparto (Lygeum spartum)	Cylindrical, thin, no striæ	Narrow	0·5–5	9–20 (13)	Greenish-yellow
Coconut (Cocos nucifera)	Cylindrical, with pores and fissures	Marked, about $\frac{1}{4}$	0·5–1	12–24 (20)	Brownish-yellow
Kapok (Bombaceæ)	Cylindrical, empty, no striæ	Very wide, about $\frac{9}{10}$	10–30	20–40 (24)	Yellow
Vegetable silks (Asclepiadeæ, Apocyneæ)	Cylindrical, empty, no striæ	Very wide, about $\frac{9}{10}$	10–60	12–90	Yellow, green edge

6. Description of Fibres of Vegetable Origin.—The most important vegetable textile fibres, which will be described below, are cotton, flax, hemp, ramie, jute, agave, pita and sisal, New Zealand flax, esparto, Manila

hemp, coconut, kapok and vegetable silks. Table LII gives, for these fibres, the principal microscopic characters utilised for their recognition and also their behaviour towards the iodine-sulphuric acid reagent.

` I. COTTON. Cotton is furnished by the down surrounding the seeds of various species of *Gossypium*. This fibre, which is unicellular and closed at only one end, is always isolated, and appears under the microscope as a ribbon twisted at intervals on its own axis like a spiral (Fig. 68, Plate VI). The wall is comparatively thin and sometimes somewhat raised like a rim ; the lumen is wide—three or four times as wide as the walls. This lumen is mostly empty, but sometimes contains granulations representing the original protoplasm in a dried state. The cotton fibre, which consists solely of cellulose, is coated in the raw state with a very thin cuticle, which is readily seen in a dry microscopic preparation. When raw cotton is treated with ammoniacal cupric oxide solution, whilst the cellulose of the fibre first swells and then dissolves, the cuticle remains almost intact, so that the fibres assume characteristic microscopic forms. The section of the cotton fibre (*see* Fig. 69, Plate VI) is elliptical, curved or reniform, with a fissure-like lumen.

In some cases, however, cotton fibres appear like thin flattened ribbons with a peculiar transparency and with occasional bruised bends (Fig. 70, Plate VI). This is so-called dead cotton and is due to faulty cultivation or to incomplete maturation.

Microscopic examination of cotton may serve, not only for its recognition, but also for the estimation of its quality, that of most value having the roundest fibres with numerous twistings. Of less value are fibres of dead cotton and those of irregular appearance, being furnished with swellings or fused together, or crooked and wrinkled or otherwise strange or with a diameter three or four times as great as the normal. Further, microscopic examination—in conjunction with treatment with ruthenium red solution (*see* Reagents, p. 442)—shows if the cotton is raw or bleached ; the fibres are treated on a slide with a few drops of the reagent and a cover-glass fitted, the liquid after a few minutes being absorbed with a strip of filter-paper and the preparation observed under the microscope. In this way crude cotton fibres are coloured red, whilst bleached ones remain colourless, this difference in behaviour being due to the presence of the cuticle on the raw cotton and its disappearance during bleaching.

2. MERCERISED COTTON. Mercerised cotton fibres under tension appear under the microscope as fairly regular cylinders with a shining surface sometimes striated longitudinally, and with an internal channel, sometimes narrow, sometimes swollen, and sometimes entirely lacking. The characteristic twistings of cotton are also absent. Here and there may be observed irregularities in the diameter of the fibre, these being constrictions which represent the points where the original fibre was twisted. The sections appear rounded with a more or less distinct central hole. ,

[Further, somewhat different characters may be observed according to the process used and especially according to the degree to which the mercerisation has been carried, intermediate stages existing between the typical forms of mercerised cotton and those of ordinary cotton.

Unstretched mercerised cotton is less characteristic and resembles more closely the original fibres. The surface is rough, with moderately frequent

longitudinal striations. The sections are oval or round with an irregularly circular central lumen, sometimes showing small radial branchings.

3. FLAX. Flax is obtained from the bast fibres of numerous varieties of Linum, the most common being *L. usitatissimum*. Under the microscope flax fibres appear (Fig. 72, Plate VI) as uniform, regular cylinders, furnished with very narrow central channels. They are almost always isolated or readily separable. One characteristic which facilitates their recognition consists of the transverse striæ or impressions, which occupy the whole width of the fibre. Sometimes these striæ are united in pairs and slightly inclined so as to resemble the letter X. Slight and short swellings are also easily observable, especially in correspondence with these transverse striations : the swellings and striæ give to flax fibres the appearance of a bamboo cane.

These swellings and markings seem to be due either to the insertion of other cells adherent to the fibre or to mechanical manipulations to which the fibres themselves have been subjected. Slight longitudinal striations are also present in some cases, but these do not prevent observation of the more pronounced middle line marking the channel. On the whole the fibres appear smooth and semi-transparent. Their ends are pointed.

The sections (Fig. 73, Plate VI) are isolated or in small, polygonal groups with five or six sides, angles mostly well defined and a central lumen which is small and circular or in the form of a short line. When the whole fibre or its section is treated with iodine and sulphuric acid, the cell walls are coloured blue, whilst the lumen is seen to contain a granular protoplasmic substance which is coloured yellow.

4. HEMP. This is obtained from the bast fibres of *Cannabis sativa*. Under the microscope these fibres, which are usually joined in bundles, have a bruised cylindrical appearance and a diameter greater than that of flax fibres (Fig. 74, Plate VII). They are irregular as regards thickness and there are many longitudinal striations, which are sometimes so marked as to render difficult the observation of the internal channel, the latter being about one-third as wide as the fibres. Transverse striæ are also observed ; often these do not traverse the whole width of the fibre and they are not so regular in appearance as with flax. At the ends the fibres are usually rounded and sometimes slit down for a short distance.

When treated with iodine and sulphuric acid, they become blue in the body of the walls, but the surface exhibits a thin lignified cuticle which is coloured yellow, so that the resultant colour of the whole fibre is greenish. The yellow cuticle is clearly seen when the cross-sections of the fibres are treated with this reagent. This character, which serves to distinguish hemp from flax, gradually disappears in fibres subjected to wear or to bleaching and washing.

In cross section, hemp (Fig. 75, Plate VII) is almost always united in groups with rounded contour ; the lumen is elongated like a fissure or cavity and sometimes subdivided or radiating, thus differing markedly from the point-like lumen of flax.

Although the typical characters of the flax fibre differ appreciably from those of hemp, certain products of these two fibres are somewhat difficult to

differentiate. Flax fibres from the middle of the stem are, indeed, uniform and slender, with the appearance of thin, isolated cylinders and with an almost capillary lumen and tapering extremities, so that they are readily distinguishable from *ordinary hemp* fibres ; there are, however, other fibres from the lower portions of the stem in which these characters are lost and others assumed which render them more like hemp in appearance. Such fibres show increased diameter and a moderately wide internal channel. These fibres are in comparatively low numbers since, owing to their shortness and decreased strength, they constitute the waste (tow) of flax.

5. RAMIE. This includes the bast fibres obtained from certain *Urticaceæ*, cultivated mostly in the Far East ; owing to their whiteness, lustre and strength they are the best textile fibres furnished by the vegetable kingdom.

Under the microscope (Fig. 76, Plate VII) they are mostly isolated, of marked dimensions and in the form of a ribbon of somewhat variable thickness. The wall is copiously and finely striated with pronounced, very deep fissures, which appear as dark lines, rather oblique to the axis of the fibre. In some cases thin fibres are detached from the walls in the form of very thin ribbons. The very wide lumen is clearly visible ; the ends are blunt and rounded, with very thick walls. The fibre consists of cellulose and is hence coloured blue with iodine and sulphuric acid.

The cross-sections are of ample dimensions and mostly isolated or united in groups of two or three ; they are elongated with a rounded contour. The full lumen follows sensibly the shape of the external outline and often contains a substance which is coloured yellow by iodine and sulphuric acid, while the wall is coloured blue and shows no lignified cuticle, although the various strata of growth of the wall are clearly exhibited. From the lumen sharply defined clefts start, these corresponding with the oblique fissures which are observed in the length of the fibre and which thus occupy the whole thickness of the wall.

6. JUTE. This is obtained from the stalk of various species of *Corchorus*. The fibres are of characteristic microscopic appearance (Fig. 77, Plate VII), since they are smooth, cylindrical, mostly united closely in bundles, and free from striation. The walls of the fibres are very irregular in thickness, so that the lumen is sometimes very wide, sometimes narrow to a mere line, and sometimes absent for some length. The ends are usually rounded or irregular. The fibre is intensely lignified (about 40% of lignin), being coloured yellow by iodine and sulphuric acid and red by phloroglucinol and concentrated hydrochloric acid.

The cross-sections (Fig. 78, Plate VII) are always combined in compact groups and have a distinct polygonal shape and a central, circular, empty lumen.

7. AGAVE, PITA, SISAL. These are derived from various species of *Agave* and are smooth, regular fibres with thin walls and a full lumen (Fig. 79, Plate VII).

They are almost always accompanied by spiral vessels and by long, narrow parenchymatous cells. The ends are wide and blunt, and the cross-sections, which are always in groups, are polygonal and closely contiguous ; the lumen also is polygonal. Owing to their pronounced lignifi-

cation, the fibres are coloured yellow by iodine reagents. The ash contains calcium carbonate crystals, sometimes well formed.

8. NEW ZEALAND FLAX. This is obtained especially from the leaves of *Phormium tenax*. The fibres are united in bundles—which are readily dis-aggregated—and are very thin, uniform and smooth, with a peculiar appearance of rigidity; the lumen is very distinct and occupies about one-third of the fibre (Fig. 80, Plate VIII). The ends are acute. The cross-sections of unbleached fibres are united in bundles which are polygonal with rounded angles; they are only weakly joined and the lumen is rounded and free from contents. By iodine and sulphuric acid, the raw fibres are coloured yellow, while bleached fibres assume a greenish or blue colour and then show marked flexibility.

9. ESPARTO, HALFA. Esparto is obtained from *Lygæum spartum*. The fibres, tightly united in bundles, are very thin and smooth, with a narrow internal channel (Fig. 81, Plate VIII), the ends being usually rounded. The cross-sections, in groups, are rounded or oval and show a very small, almost point-like lumen. When treated with iodine and sulphuric acid, some of the fibres are coloured yellow, whilst others, of more recent formation, become blue or pale violet.

Very similar to these are fibres of Halfa (*Stipa tenacissima*). The two kinds may be differentiated by means of the hairs of the leaves from which the fibres are derived, these being found among the fibres. With esparto these short hairs are somewhat rounded with thin walls and wide lumen, whilst those of halfa terminate in a sharp point and have fairly thick walls and a narrow lumen.

10. MANILA HEMP. These consist of bundles of fibres from the leaves of various Musaceæ, especially *Musa texilis*. The fibres, which are wholly lignified, are smooth and regular, with a wide and distinct lumen (Fig. 82, Plate VIII); the ends are usually sharp. The cross-sections, which are in groups, have a polygonal outline with very rounded angles and a distinct lumen. Manila hemp may be distinguished from other fibres by the characteristic presence of small cells which are united in series and adhere to the bundles of fibres and, being very rich in silica, retain their original form even after incineration of the fibres.

These siliceous residues have a clearly marked central cavity which causes them to resemble a string of pearls; they are rendered especially clear under the microscope by treating the ash on a slide with a drop of dilute hydrochloric acid or by macerating it in chromic acid. Being entirely lignified, these fibres are coloured yellow by the iodine-sulphuric acid reagent.

11. COCONUT FIBRE. This is obtained from the husk of the fruit of *Cocos nucifera*. The reddish fibres, which are tightly bound in bundles, are short and stiff, with walls rendered irregular and of varying thickness by frequent pores, channels and fissures; the channel is wide, its diameter being greater than the thickness of the walls. The ends are always blunt and the cross-sections, which are in groups, have rounded polygonal forms and show clearly the wide internal cavities. By iodine-sulphuric acid they are coloured yellowish-brown. The fibres also are accompanied by other

cells rich in silica, which can be observed in the ash, under a high magnification, in the form of minute pearls.

12. KAPOK (VEGETABLE WOOL). This comprises the down surrounding the seeds of certain of the *Bombaceæ*. These fibres, which closely resemble one another, appear isolated, and have a slightly conical, cylindrical form and very slender, lignified walls (Fig. 83, Plate VIII). The lumen is wide, occupying the greater part of the width of the fibre, and is full of air ; the cross-sections are sensibly circular.

13. VEGETABLE SILKS. These are derived from various plants of the genii, *Apocyneæ* and *Asclepiadeæ*, and are remarkable for their peculiar lustre. The fibres, which are sometimes yellowish or reddish, are unicellular and appear as empty cylinders with very thin walls. Sometimes they exhibit at the base a characteristic reticulate aspect. The walls are lignified.

7. Fibres of Animal Origin.—Textile fibres of animal origin are principally sheeps', goats and camels' wool, that of certain Camelidæ, ordinary silk and wild silk. Table LIII gives the main microscopic characters used for their recognition.

1. WOOL. Wools and the hair of animals in general appear under the microscope (Fig. 84, Plate VIII) to consist, in their normal and complete structure, of three layers, namely : a central *medullary canal*, surrounded by a layer of very thin *fibrillary cells*, the latter being enveloped by wide, scale-like cells, which form the *cuticle* or *epidermis*.

Wool used in the textile industry is, however, usually free from the medullary canal, so that, in the microscopic examination, attention is turned especially to the external layer of scale-like cells, which are strongly fitted one into the other so that a considerable proportion of the surface is covered. This character has an intimate bearing on the value of the wool, since the more the scales cover one another the more are the underlying layers protected and the more resistant the fibres. This is verified particularly with the thinner fibres. The superposed scales, like fish-scales, exhibit a free edge always turned towards the tip of the fibre. Owing to this free edge the scales of different fibres may, when these come into intimate contact, become interlocked, the wool thus " felting." In some wools, especially goats' and camels', the scales are so thin and transparent as to allow a clear view of the fibrous layer beneath, this then assuming considerable importance as regards the recognition of the wool.

Finally, since the great bulk of wool is obtained by shearing, which is repeated several times on the same animal, it is not easy to find the natural point of the fibres, a sharp section due to the cutting being found instead.

In examining wool it is sometimes of importance to note the uniformity and number of the undulations of the fibre. This number, which normally increases with the fineness of the wool, is referred to 1 cm.

The more common wools of commerce are as follows :

(a) *Sheeps' wool*. Under the microscope this fibre exhibits the form of slender cylinders on the surface of which appear more or less oblique, fine, irregular striæ, representing the edges of the epidermal scales. In general, two of these cells or scales are sufficient completely to surround

TABLE LIII

Microscopic Characters of Animal Fibres

Fibre.	Microscopic Appearance		Diameter, μ.
	of the Fibre.	of the Channel.	
Ordinary sheeps' wool	Cylindrical (with scales)	Absent	25
Merino wool . . .	Cylindrical (with scales)	Absent	23–27
Angora wool . . .	Cylindrical (with scales), longitudinal striation	Absent	Fine, 21–23; medium, 45
Camels' hair (fine) .	Cylindrical, scales very evident, longitudnal striations with granules and linear masses of pigment	Often present, granular in the form of islands.	20–30
Camelidæ (vicuna) wool	Cylindrical, scales not very evident, longitudinal striations with fine granulations of pigment	Thin, often interrupted	18–20
Rabbit's hair . .	Cylindrical, scales not very evident, no longitudinal striation	Full, interspersed with empty spaces, sometimes multiple	14–16
Hair (women's) . .	Cylindrical, scales scarcely visible, longitudinal striæ, very fine granulations of the pigment, without accumulations	Mostly absent	60–80
Ordinary silk . .	Cylindrical, transparent	Absent	13–14
Wild silk	Ribbon-like with clear, longitudinal striæ and transverse bundles	Absent	Mylitta 32 Yama-mai 40

the fibre, the outline of which appears slightly toothed. The fibrous layer is not very distinct and the medullary canal is absent, being encountered only in the coarser wools.

The most important sheeps' wool is that of the Merino, remarkable for its thinness and for the great distinctness of the epidermal scales, which are cylindrical or semi-cylindrical. Since these scales have a very pronounced free edge, the fibre appears to have a toothed outline and the fibrous layer below is sometimes faintly apparent as a delicate longitudinal striation. The medulla is always lacking.

(b) *Shoddy.* It is well known that in the manufacture of woollen fabrics use is made not only of natural wool direct from the sheep but also of wool recovered from old yarn, fabrics, etc., this being termed shoddy. Wool may indeed be thus recovered several times. The attrition caused by wear and washing naturally modifies the superficial parts and afterwards the inner layers of the fibres, the structure of the latter as well as the strength and elasticity being changed.

In fact, microscopic examination of a woollen fabric, especially if carded, often reveals the presence of a considerable proportion of fibres which do not show the finely toothed outline and the sharply cut ends of natural wool fibres but have evidently undergone profound change (Fig. 86, Plate IX). These fibres may be free from scales either entirely or for more or less of their length, or the scales may be so worn as to be visible only with difficulty. Further, owing to the loss of the outer scales and consequent wearing of the lower fibrous layer, such fibres, which are sometimes very short (scarcely 1–2 mm.) and of irregular diameter, exhibit ends split like a brush.

Other useful indications of the presence of shoddy are, firstly, small numbers of cotton fibres and, secondly, wool fibres which show various colours not related to the general colour of the fabric.

(c) *Angora wool.* This wool, known commercially as *mohair*, is characterised by the fact that the fibrous layer, always devoid of granulations, shows through the epidermal scales, so that the fibre appears to be finely striated longitudinally. In this fine striation are somewhat wider fissures, distributed fairly regularly. The epidermal scales are not equally apparent in all the fibres. The wider fibres have a highly developed medulla (Fig. 87, Plate IX).

(d) *Camels' wool.* This consists of the hairs of *Camelus castrianus.* The more slender woolly ones of a deep yellow colour are seen under the microscope to be very thin (mean diameter, about 20 μ) and are sometimes provided with a granular medulla which is about one-third as wide as the fibre and is interrupted so as to give it an island-like formation. The epidermal scales are somewhat obliquely cylindrical and owing to their tenuity and transparency are not easily visible, especially in the darker fibres. Hence the hairs appear not with indented edges but as smooth cylinders. The fibrous layer on which the colouring pigment is scattered in linear heaps is, however, evident.

The coarser hairs, usually of a darker colour, are covered with fine, serrated, flattened scales, but these are not very distinct. The fibrous layer is always evident and shows scattered linear heaps of pigment. The medulla is appreciably developed and forms an inner cylinder, which follows a rather irregular course and has granular contents.

Very similar characters are shown by the hair of the *Cammello dromedario*, with which, however, the medullary canal is more continuous, uniform and full, occupying about one-half of the thickness of the fibre.

(e) *Wool of Camelidæ* (*vicuna*, etc.). These wools are obtained from various semi-wild or domestic animals, living mostly in South America, the principal ones being the *llama, guanaco, vicuna* and *alpaca.* Certain of these wools are highly valued for their softness, fineness and lustre.

Under the microscope these wools appear very similar ; the epidermal scales are not readily visible, but the fibrous layer is easily seen in the form of a fine striation on which is deposited a finely granular pigment. Some of the hairs, even the slender ones, exhibit a medulla, which is always very narrow and often interrupted. The finest of these wools is that of the vicuna (Fig. 89, Plate IX), which has a mean diameter of about 20 μ.

2. RABBITS' FUR. The more slender hairs of the rabbit (*Lepus cuniculus*) exhibit a characteristic appearance, owing especially to the medullary layer which presents the appearance of a succession of small, pigmented rectangles, separated by empty spaces of about the same dimensions. In the larger hairs, the medullary stratum may be composed of two or more series of cells arranged as just described. The scales, although thin, are plainly evident, but the mean fibrillary layer is scarcely visible.

3. HAIR. Figure 91 (Plate IX) represents women's hair, the scales of which are so thin as to be barely visible. The most evident feature is the fibrous layer, on which are distributed homogeneously very fine pigmentary granulations without those more or less linear masses commonly observed in other animal hair. The medulla is almost always lacking, and when it does exist, it is finely granular with a rather irregular course; it is somewhat slender, being rarely one-fourth as wide as the hair.

Tresses of Chinese hair are often found on the European market; in these the medullary canal is of more frequent occurrence.

4. NATURAL SILKS. Many lepidopterous insects secrete from special glands a liquid which becomes solid in the air in the form of filaments destined for the construction of the cocoons in which the insects pass one stage of their existence. Ordinary silk is derived from *Bombyx mori*, and wild silk from other insects (*Antheraea mylitta, A. Yama-mai*), which live wild particularly in India, China and Japan.

(*a*) *Ordinary raw silk.* The filament as produced by the silkworm is seen under the microscope to consist of two distinct fibres (fibroin) wound round and covered with a single, irregular coating; owing to its lack of elasticity, this coating or membrane (sericin) appears broken or wrinkled at many points (Fig. 92, Plate X). This structure is also shown by the cross-section of the filament, the sections of the separate fibres being seen joined and surrounded in pairs by the sericin membrane (Fig. 93, Plate X).

(*b*) *Ordinary silk.* The silk of ordinary yarns and fabrics has been deprived more or less completely of the sericin coating, so that the separate filaments are liberated. Under the microscope they appear as slender, uniform, smooth, shining, full cylinders, without channel or striation; only here and there is slight constriction or swelling observable (Fig. 94, Plate X). The sections appear isolated and somewhat triangular, with very rounded angles (Fig. 95, Plate X).

Although apparently quite smooth and homogeneous, the fibres of ordinary silk show, when examined with a high magnification and with the aid of special disaggregating reagents, very fine longitudinal striation due to the fibrillary structure proper to all silks. This structure is especially apparent in wild silks even under a low microscopic power.

(*c*) *Wild silks.* The microscopic appearance of these silks is highly characteristic, so that their recognition and their distinction from ordinary silk and from other textile fibres are easy. They form fairly wide ribbons characterised by very fine striation due to their fibrillar structure, which is rendered thus evident because the separate fibrils are not perfectly adherent and form very slender canals full of air (Fig. 96, Plate X). These silks are

characterised also by wide, oblique, transverse bands paler in colour than the rest of the fibre.

The cross-sections (Fig. 97, Plate X) have the form of flattened triangles, and show clearly the fibrillar structure and the air-channels separating the fibrils, these channels being wider in the central parts of the section.

(d) *Weighted silk*. In order to compensate for the loss due to degumming and to increase the weight, silk is often incorporated with a larger or smaller proportion of vegetable substances, but more especially with mineral salts, the most common being those of tin, zinc and aluminium.

Microscopically, weighted silk is distinguished especially by its greater diameter, while sometimes the incrustations of the added weighting material may be observed. Further it is easy to see the disaggregation of the silk into the separate fibrils constituting the filament of fibroin. If it is desired to eliminate these weighting materials in order to observe the fibre better under the microscope, the silk is treated in the manner indicated later (*see* p. 460).

5. ARTIFICIAL SILKS. This is the name given to artificial fibres which have a lustre similar to that of silk but are, however, greatly inferior to it otherwise, especially as regards strength. According to the prime material of which they are composed, they may be divided into the four following groups :

(1) The basic substance of the fibre is nitrocellulose (pyroxylin) : Chardonnet, Vivier, Lehner and Cadoret artificial silks.

(2) The basic substance is pure, non-nitrated cellulose : in this are the silks obtained by the Langhans, Pauly, Despaissis, Dreaper and Tompkins, Fremery and Urban, and Bronnert processes.

(3) The basic substance is viscose (cellulose xanthate), suggested by C. H. Stearn and manufactured by the Cross and Bevan method.

(4) Other artificial silks are made with animal gelatines by the Millar and Hummel processes (Vandura silk), but these are now of no commercial importance.

Artificial silks have a characteristic microscopic appearance which renders easy their distinction from other fibres in general and from ordinary silk in particular. The principal difference is the large diameter, but it must be borne in mind that when preparations are made in water, as is usually the case, the fibres swell considerably.

(a) *Chardonnet silk*. This appears in the form of isolated filaments, which show longitudinal striations and are sometimes rather flattened. A high magnification shows that the fibre is traversed, not by striæ, but by numerous furrows of various shapes and lengths, the fibres thus differing one from another. These furrows, which are seen more clearly in the cross-sections, are due not to the shape of the orifice through which the filament passes but rather to irregular contraction ; on this account also the sections of this silk vary in size. No value can be fixed for the thickness—this holds in general for all artificial silks—since these fibres are sold with different diameters according to the purposes for which they are to be used.

(b) *Lehner silk*. This resembles Chardonnet silk in its microscopic appearance, but contains more striæ and furrows, which are sometimes so

deep as to appear like more or less eccentric channels (Fig. 99, Plate XI).
The presence of air-bubbles scattered throughout the mass of the fibre is,
however, easily seen. The transverse sections are fairly characteristic
and show clearly the furrows and the pseudo-canals, the outline being
markedly sinuous (Fig. 100, Plate XI).

(c) *Bronnert silk.* This silk is of very uniform appearance, consisting
of rather flat cylinders which are smooth and solid and sometimes very
slightly striated ; the cross-sections are sensibly circular (Fig. 101, Plate XI).

(d) *Viscose silk* (Cross and Bevan). This is moderately uniform in its
microscopic appearance, which is that of a somewhat flattened cylinder.
It shows only fine and rare striation (Fig. 102, Plate XI). The transverse
sections are rounded rectangles (Fig. 103, Plate XI).

2. Chemical Examination

The chemical tests include : Determination of the moisture and ash
detection and determination of the dressing, qualitative test of the nature
of the fibre, quantitative determination of the different kinds of fibre in
the sample, investigation of the nature of the dye and of its fastness, deter-
mination of the nature and extent of the waterproofing, detection and
estimation of the weighting of silk, and distinction between certain crude
and bleached products. The methods used are as follows.

1. Determination of the Moisture.

(a) IN THE LABORATORY. About 5 grams of the product, taken in the
case of a fabric as indicated on p. 462, are weighed exactly in a tared, per-
fectly tight weighing bottle. The weighed sample (p) is then spread on a
sheet of paper in an air-oven and heated for 3–4 hours at 100–105° C. ; it
is then placed in the weighing bottle and left in the oven at the same tem-
perature for about two hours further. The weighing bottle is then left for
about half an hour in a desiccator and weighed rapidly. The sample may
be heated in the oven for another period of 2–3 hours and again weighed.
The loss of weight (p') represents the moisture.

(b) The commercial weights of consignments of fibre or yarn are now
determined in special " *conditioning* " establishments. This weight is
obtained by adding to the weight of the dried product (absolute weight) a
certain percentage of moisture recognised as normal in the ordinary dry
fibre. At first the above establishments were concerned solely with silk,
but nowadays other textile materials and yarns are examined, especially
wool and cotton.

The percentages of moisture chosen as normal—which require revision
in some cases, especially with wool—are as follows :

Raw wool	16%
Combed wool in tops, raw	19
Do. do. washed	18·25
Carded wool	17
Silk	11
Cotton	8·5
Flax and hemp	12
Jute	13·75

1. *Conditioning of silk.* The conditioning of silk is carried out as follows :

The gross weight of the package and the weight of the packing are determined, the difference representing the net weight of the silk. From different parts of the bale a number of skeins, weighing altogether 750–1500 grams, are taken, the whole being divided into three approximately equal parts and each of these placed in a suitable vessel, which is immediately closed. Each of the three parts is immediately weighed exactly. The succeeding operations need not be carried out at once, but may wait their turn, since the bulk weight of the silk is known and the samples taken have the proportion of moisture originally present. Of the three samples, two are weighed separately in the dry state by means of the apparatus described below, while the third is kept in reserve as a control in case of need.
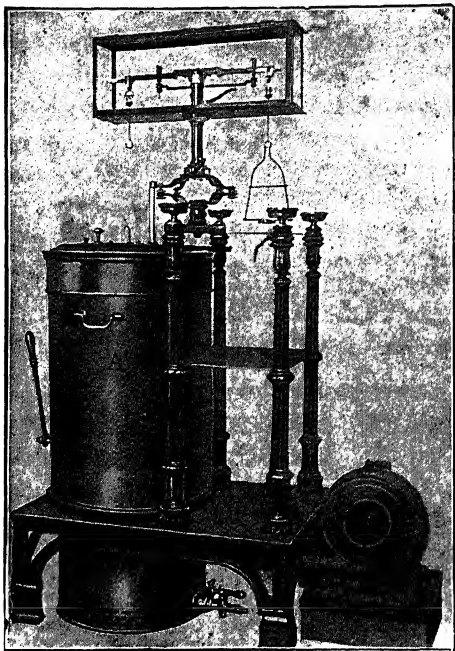
The apparatus mostly used is that of Corti of Milan (Fig. 104). The sample to be conditioned is placed in an aluminium vessel open at the top and having a base of aluminium wire gauze. This vessel can be attached to the lower part of a cylindrical rod which is situate in an air-oven (A) ; the upper part, which protrudes from the oven, may be connected with one of the arms of a balance. The heating is effected by means of a current of hot air which is aspirated through the oven and consequently through the yarn under a pressure slightly above 15 mm. of water and at the rate of 2·5 cub. m. per minute. With this apparatus the sample is rapidly dried

FIG. 104

to constant weight. The air is admitted to the drying chamber at 140° C. The apparatus is provided with perfectly tight valves so that during the weighing the influx of air is completely intercepted.

If the difference between the results obtained with the two samples does not exceed 0·3%, the commercial weight is calculated from the sum of the two original weights and that of the absolute weights. If the difference is between 0·3 and 1%, the absolute weight is determined on the third sample and when the maximum difference in the three tests does not exceed 1%, the commercial weight is based on the three original weights and the three absolute weights, summed separately ; if this is not the case, fresh samples are taken and the tests repeated.

The *commercial weight* of the consignment is then calculated as follows : On the basis of the sum of the original weights and the sum of the absolute

weights of the samples and the net weight of the consignment, the absolute weight of the latter is calculated. To this is added the moisture at the rate of 11%, the commercial weight being thus obtained.

EXAMPLE :

Gross weight	104·82 kilos
Tare checked	1·21 ,,
Net weight	103·61 ,,

21 skeins were taken, and 14 of them, having the original weight 975·80 grams, reduced to the absolute weight 872·70 grams. Hence

The above net weight corresponds with the absolute weight	92·66 kilos
Increase of 11% on 92·66.	10·19 ,,
Commercial weight	102·85 ,,
This represents a decrease of 0·73%	0·76 ,,
Original net weight	103·61 ,,

When, for certain purposes, the spinner or weaver has recourse to the use of a dressing (with a basis of vaseline, glycerine, soap, fatty matter, borax, or other substance), crude dressed silk is obtained which loses part of the dressing besides water during the conditioning. When the silk is heavily dressed and the dressing consists of readily volatile substances, the diminution in weight at the expense of the dressing may be appreciable. To ascertain what this extra diminution in weight during conditioning has been, it would be necessary to determine chemically the proportions of extraneous matters present in the silk before and after the conditioning test and to take the difference between these two results.

2. *Conditioning of artificial silk.* This is carried out at 120° C.

3. *Conditioning of wool.* The conditioning of wool or of the corresponding yarn is made at 110° C.

4. *Conditioning of cotton.* For raw cotton and the corresponding yarn the conditioning is carried out at 105–110° C., the value 8·5% being adopted for the moisture. For yarns twisted wet special agreements are made. As regards sampling, three or four skeins from each bale or nine or ten cops from each case are taken. The samples are placed in suitable air-tight vessels—which should be filled if possible—these being then dispatched to the conditioning house together with a statement of the weight of the consignment. If the conditioning test shows more than 12% of moisture, the material may be refused.

With wool and cotton and the corresponding yarns and also with artificial silk, the maximum difference allowable between the results of the conditioning tests of the first two samples is 0·5%. If the difference exceeds this proportion but not 1%, the third sample is also conditioned, and when the sum of the differences between the results of the three tests does not exceed 1%, the original weights and the corresponding absolute weights of the three samples are taken as the basis of the commercial weight. In the contrary event, the treatment of the three samples is repeated. The calculation of the commercial weight is made as with silk, the proper normal moisture value being taken in each case.

2. Determination of the Ash.—About 5–10 grams of the product are heated in a tared dish, at first over a small flame, which is then gradually

increased. The incineration is completed in a muffle at a dull red heat, the dish being allowed to cool in a desiccator and weighed.

With *silk* the *alkalinity of the ash* is usually determined, the ash being lixiviated with 400 times its weight of boiling distilled water and the alkalinity of the aqueous extract thus obtained expressed as sodium oxide per 100 parts of dry silk.

3. Investigation and Determination of the Dressing.—Numerous substances are used for the dressing of yarns and fabrics, this constituting the surface which either gives to the product some particular appearance (opacity, transparency, moiré effect, etc.) or renders it more or less stiff. The chief of these are: flour, starch, dextrin, gum, vegetable gelatines, fats, oils, soaps, wax, paraffin wax, stearin, glycerine, glucose, borax, calcium or magnesium chloride, ammonium salts, kaolin, lead, calcium and barium salts, etc.

The products most often prepared, sometimes with considerable quantities of dressing, are those of cotton. Silk fabrics are also heavily dressed, but in this case it is not a mere superficial layer of extraneous matter, since the substances constituting the so-called *weighting* of silk are, partially at least, incorporated in the fibre (*see* later: Weighting of Silk).

In general, the dressing of cotton goods may be removed by boiling the fabric with water and rubbing it thoroughly between the hands. The dressing is thus detached and partly dissolves in the water (dextrin, glucose, glycerine, gum, soluble mineral salts), partly remains emulsified (fats, paraffin wax, starch) and partly settles to the bottom of the water (kaolin, insoluble mineral salts). Thus, the different substances composing the dressing may be detected in the water. Non-volatile salts may also be sought in the ash of the fabric. It must, however, be borne in mind that the ash of dyed goods may also contain metallic oxides from salts used as mordants (salts of copper, chromium, iron, antimony, tin, aluminium, etc.), which are not removed merely by boiling with water and rubbing.

For a systematic investigation, it is well first to dry the sample in an oven at 105° and to extract it with ether in a displacement apparatus, the ethereal extract being tested for fats, wax and paraffin wax; the fabric is then boiled with water and rubbed between the hands, the liquid being subsequently tested for the above salts.

For the *quantitative determination* of the dressing, for instance, in cotton fabrics, the following method may be used:

The moisture is determined in 5 grams as indicated on p. 455.

Another piece of the fabric weighing about 5 grams or the dried piece, if this is not wanted for another purpose, is well soaked in water and then wrung between the hands to expel excess of moisture and immersed in 100 c.c. of a 0·1% solution of crystallised sodium carbonate previously brought to gentle boiling in a beaker. The boiling is continued for exactly 15 minutes, the beaker being then removed from the flame, the liquid poured away and the fabric washed two or three times by decantation with hot distilled water. The washing is finished under a water-tap, the material being rubbed softly and carefully between the fingers.

Meanwhile 100 c.c. of 3% hydrochloric acid (3 c.c. of concentrated HCl of

sp. gr. 1·19 in 100 c.c. of distilled water) are heated in another beaker and when the liquid begins to boil, the washed fabric is immersed in it. The beaker is then left for 15 minutes on a briskly boiling water-bath, the acid being afterwards poured off and the goods washed two or three times by decantation with hot water and finally under a water jet. The fabric is then returned to the beaker and shaken with absolute alcohol, the latter being poured off, a fresh quantity added, and the material pressed between the fingers; in all not more than 50 c.c. of alcohol are used. The fabric is next washed and pressed with a little ether, dried in an air-oven at 100–105° C. for about 2 hours and weighed. The loss of weight represents dressing plus moisture.[1]

If the proportions of cotton and of dressing in the state in which it occurs in the fabric are required, the moisture is distributed in proportional parts between the cotton and dressing. Also, if necessary, the quantity of dressing relative to 100 parts of raw fabric may be calculated.

EXAMPLE : 5 grams of material lost 0·347 gram at 100–105° C. Moisture = 6·94%.

5 grams, treated with sodium carbonate and then with hydrochloric acid, etc., lost 1·052 grams. Dressing + moisture = 21·04%.

Hence :

(a) Moisture . . . . . . 6·94%
(b) Dry dressing . . . . . . 14·10
(c) Dry cotton . . . . . . 78·96

Distribution of the moisture between dressing and cotton is calculated as follows :

$$(100 - a) : a :: b : x \text{ (moisture in the dressing)}$$

i.e., $93·06 : 6·94 :: 14·10 : x,$

so that, $x = 1·05.$

The dressing and the corresponding moisture will therefore be :

$$14·10 + 1·05 = 15·15$$

and the cotton and its moisture,

$$100 - 15·15 = 84·85.$$

Finally, the dressing referred to 100 parts of raw fabric will be given by the proportion,

$$84·85 : 15·15 :: 100 : x$$
$$x = 17·81$$

4. Investigation of the Nature of the Fibres.—The aim of this investigation is to differentiate between groups of fibres, e.g., between animal and vegetable fibres or between certain given fibres. Preliminary microchemical tests are usually made in order to limit the field of investigation to a given group of fibres; in some cases such tests are used to confirm conclusions drawn from the microscopic appearance of the fibres.

With highly coloured or dressed goods, it is well first to eliminate as much as possible of the colouring and dressing materials by the treatment indicated on pp. 458 and 460 in reference to the detection and determination of the dressing and of the weighting of silk.

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[1] The treatment described eliminates all the dressing from the fabric, but at the same time it removes also a part of the colouring matter (if the material is dyed), which is however usually small in amount.

The tests more commonly applied are as follows:

1. DISTINCTION BETWEEN ANIMAL AND VEGETABLE FIBRES.

(a) If a little of the sample, when brought near to a flame, burns with an odour of burnt horn and leaves a spongy carbonaceous residue adhering to the unburnt part of the fibre, it consists of animal fibres. If, however, it burns rapidly with emission of an empyreumatic odour and leaving no carbon but only a slight ash, it is composed of vegetable fibre.

Heavily weighted silk sometimes burns like vegetable fibres and leaves a considerable amount of ash containing mostly oxides or salts of tin, or oxide of aluminium or iron; if, however, a large portion of the sample is taken, the odour of burnt horn may also be observed in some cases. In doubtful cases the weighting may be removed as far as possible from a portion of the product and the burning test repeated. The weighting material is removed (1) by heating the fibre at 60° with 2% sodium carbonate solution and then at the same temperature with 5% potassium bioxalate solution, (2) by treatment with 3% sodium sulphide solution and then with 2% hydrochloric acid, or (3) by heating with 1–2% hydrochloric acid at 60° and then with 2% sodium carbonate solution at 80°. When the fibre is largely freed from dressing, weighting and colour, it exhibits normal characters and emits an odour of burnt horn.

(b) A little of the sample is boiled for a few minutes with 10% caustic potash solution, which dissolves animal but not vegetable fibres.

2. DISTINCTION BETWEEN NATURAL AND ARTIFICIAL SILK AND BETWEEN THE DIFFERENT ARTIFICIAL SILKS (A. Solaro).

(a) When brought near to a flame, natural (ordinary and wild or tussah) silk burns with an odour of burnt horn and leaves a spongy carbonaceous residue (except with heavily weighted silk); artificial silks with a cellulose basis burn rapidly, almost without odour or residue, while " strengthened "[1] silks leave an ash in the form of the fibre; artificial silks with a gelatine basis (A. Millar's silk, Vandura silk) burn like animal fibres.

(b) A portion of the sample is immersed in the cold in concentrated hydrochloric acid or in sulphuric acid of 58° Baumé: ordinary non-weighted, natural silk dissolves readily, heavily weighted silk and wild natural silk more slowly; artificial silks dissolve after some time, those with a gelatine basis first softening and then dissolving in about two hours.

(c) A little of the sample is heated to boiling with 10% caustic potash solution: non-weighted natural silks dissolve promptly and weighted silks or raw wild silks after some time, while artificial silks, except those derived from gelatine, do not dissolve.

(d) Some of the sample is boiled with zinc chloride solution of 60° Baumé (for preparation, see p. 464): natural silks, white or dyed or weighted, and artificial silks with a nitrocellulose basis, dissolve in a minute; weighted silk dyed black and artificial cellulose or viscose silks dissolve in about $1\frac{1}{2}$ minute, whilst wild silks require several minutes for complete solution.

(e) A portion of the sample is immersed in cold Löwe's solution (see p. 464): natural raw silk dissolves in ten minutes, whereas weighted silk

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[1] Artificial silks are sometimes strengthened by immersion in a bath containing 1–10 parts of formaldehyde and 90–99 parts of acetic acid (40 %).

and especially wild silk are not completely dissolved even in two hours; artificial silks are not dissolved, excepting those made from gelatine, which soften and dissolve after some time.

(*f*) A little of the sample is dissolved in pure concentrated sulphuric acid and a crystal of diphenylamine sulphate added to the solution: with artificial silks based on cellulose nitrate, a blue coloration is obtained. This test is applicable only to undyed fibres.

3. DISTINCTION BETWEEN WOOL AND SILK.

(*a*) A little of the sample is dissolved in 10% caustic potash solution and a few drops of sodium nitroprusside added: wool gives a violet, silk no coloration.

(*b*) A portion of the sample is boiled for some minutes with zinc chloride solution of 60° Baumé (*see* p. 464), which dissolves silk but not wool.

4. DISTINCTION BETWEEN HEMP AND JUTE.

(*a*) By phloroglucinol solution (1 gram phloroglucinol, 12·5 c.c. of alcohol, 2·5 c.c. of concentrated HCl) jute is coloured red after a few moments, whereas hemp is coloured only a very faint pink.

(*b*) By nitric acid containing nitrous vapours, hemp is coloured yellow, jute blood-red.

5. DISTINCTION BETWEEN FLAX AND HEMP.

The product is treated as follows: A 3% crystallised sodium carbonate solution, heated to 90–95° C., is poured in successive small quantities on to a little of the samples, each quantity being decanted off; the fibre is afterwards left immersed for about half an hour in the same solution, which is allowed to cool, and is then washed and carefully rubbed in water and left to dry in the air. The dry sample is next dipped repeatedly into cold petroleum ether and vigorously rubbed each time between the hands, the petroleum ether being renewed several times during the treatment. It is then left exposed to the air for some hours.

By means of a penknife the ends of a few fibres or threads of the sample treated as above are unravelled with a penknife and then held firmly at one end and combed out on a board (not too hard) with a metallic spatula furnished with fine points bent backwards. In this way the bundles of fibres are decomposed as completely as possible into their elements. The end thus separated into fibres is then carefully scraped with a penknife in the way used for microscopic preparations. The fibres freed in this way from the coarser elements are united, spread out and heaped up by means of needles, these operations being repeated two or three times; they are finally pressed together gently with the finger so as to obtain a homogeneous and compact tuft. The loose ends are cut off with small scissors, the tuft being given an almost circular form, the diameter being about half a centimetre and the thickness about a millimetre. The tuft of fibres thus prepared is placed carefully by means of a needle on a mixture of water and alcohol (25 c.c. of absolute alcohol made up to 100 c.c. with distilled water) contained in an ordinary weighing bottle and kept at a temperature of 20–22° C. *Hemp* fibres rapidly become wetted with the liquid and when shaken, even gently, *sink to the bottom*; those of *flax* become wetted only slowly and *float* on the surface even if the liquid is shaken.

5. Quantitative Determination of the Different Fibres in Mixed Fabrics.—The aim of this determination is to ascertain the quantities of the various fibres constituting a fabric, e.g., the quantities of wool and cotton in a flannel, or the quantity of silk in a mixed fabric containing this fibre, etc.

Two methods are available : By unravelling, and by chemical means. The first is the simpler and more certain method and consists in separating mechanically the threads of different types and weighing each separately. This method may be used only when the weft and warp are each composed of only one textile material, e.g., when the weft is wool alone and the warp cotton alone.

In all cases when the fabric does not fulfil such condition, as, for instance, with fabrics made with mixed yarns, in those with silk interwoven, etc., or when the fabric cannot be unravelled, the analysis must be made by chemical means, the various fibres being separated by suitable solvents.

In some cases the two methods may be used simultaneously. For instance, where it is possible to separate mechanically the threads of the warp from those of the weft and only the former are of mixed yarn, these alone need be subjected to analysis by chemical means.

(*A*) UNRAVELLING METHOD. A piece of the fabric, cut exactly along the warp and weft threads and without ragged edges, is weighed. With worked tissues, brocaded, embroidered and the like, the sample must be so cut that it represents the whole design or a proportional part of it. The fibres of different kinds are then separated with suitable tweezers, collected in tared weighing bottles and weighed.

(*B*) CHEMICAL METHOD. *General :* Chemical analysis gives the various fibres composing a fabric in the dry state, so that it is necessary to determine, besides the fibres, also the moisture, the dressing and the colouring matter. When the percentage composition of the fabric is known—dry fibres (wool, cotton, etc.), moisture, dressing and colour—calculation of the composition in yarns, as is obtained by the mechanical method, requires the proportional distribution of the dressing and colour to the different fibres, and the distribution of the moisture found to the fibres in accordance with so-called coefficients of *normal moisture*. These have the following values (Solaro).

	Referred to 100 parts of Fibre.	Referred to 100 parts of Dry Fibre
Cotton	7·50	8·11
Wool	11·00	12·36
Silk	8·50	9·29
Black, weighted silk	12·00	13·64
White or coloured weighted silk	9·00	9·89

Calculation of the composition of a fabric from the data given by chemical analysis is carried out as follows :

Let : U = percentage of total moisture

A = percentage of dressing and colour, together

f_1, f_2, f_3 = percentages of pure dry fibres

a_1, a_2, a_3 = dressing and colour for each fibre

u_1, u_2, u_3 . . = moisture for each fibre

k_1, k_2, k_3 . . = coefficients of normal moisture percentage of dry fibre

x_1, x_2, x_3 . . = percentage of each fibre in the fabric with its own dressing and moisture.

Then:

1. The dressing and colour for each of the fibres are given by:

(I)
$$a_1 = \frac{A f_1}{100 - U - A}$$

$$a_2 = \frac{A f_2}{100 - U - A}$$

$$a_3 = \frac{A f_3}{100 - U - A}.$$

2. The moisture to be distributed to each of the fibres will be given in the case of two fibres, by the formulæ:

(II)
$$u_1 = \frac{U f_1 k_1}{f_1 k_1 + f_2 k_2}$$

$$u_2 = \frac{U f_2 k_2}{f_1 k_1 + f_2 k_2},$$

and, in the case of three fibres, by the formulæ:

(III)
$$u_1 = \frac{U f_1 k_1}{f_1 k_1 + f_2 k_2 + f_3 k_3}$$

$$u_2 = \frac{U f_2 k_2}{f_1 k_1 + f_2 k_2 + f_3 k_3}$$

$$u_3 = \frac{U f_3 k_3}{f_1 k_1 + f_2 k_2 + f_3 k_3}.$$

3. The percentage of each fibre in the fabric, with its dressing, colour and moisture, will be given by:

(IV)
$$x_1 = f_1 + a_1 + u_1$$
$$x_2 = f_2 + a_2 + u_2$$
$$x_3 = f_3 + a_3 + u_3$$

If it is not necessary to know the dressing and moisture separately for each fibre, the quantities of the fibres with their dressing, colour and moisture may be obtained directly by the following formulæ in the case of two fibres:

(V)
$$x_1 = \frac{f_1 (100 - U)}{100 - U - A} + \frac{U f_1 x_1}{f_1 k_1 + f_2 k_2}$$

$$x_2 = \frac{f_2 (100 - U)}{100 - U - A} + \frac{U f_2 k_2}{f_1 k_1 + f_2 k_2}$$

or by the following in the case of three fibres:

(VI)

$$x_1 = \frac{f_1 (100 - U)}{100 - U - A} + \frac{U f_1 x_1}{f_1 k_1 + f_2 k_2 + f_3 k_3}$$

$$x_2 = \frac{f_2 (100 - U)}{100 - U - A} + \frac{U f_2 k_2}{f_1 k_1 + f_2 k_2 + f_3 k_3}$$

$$x_3 = \frac{f_3 (100 - U)}{100 - U - A} + \frac{U f_3 k_3}{f_1 k_1 + f_2 k_2 + f_3 k_3}.$$

The application of these formulæ is illustrated in the examples given later.

Reagents : The reagents necessary for the quantitative analysis of fabrics by chemical means are as follows :

1. A 0·1 % aqueous solution of crystallised sodium carbonate.

2. Sulphuric acid of 58° Baumé (1000 c.c. of pure concentrated acid of 66° Baumé in 530 c.c. of distilled water).

3. 10 % caustic potash solution.

4. Zinc chloride : 100 grams of the salt are dissolved in 80 c.c. of water, 4 grams of zinc oxide being added and the liquid heated for about an hour on a water-bath with frequent agitation ; when cold, the solution is filtered through asbestos or glass wool. The solution should be of 60° Baumé and, if this is not the case, it is diluted or concentrated to bring it exactly to this density.

5. Löwe's solution : 16 grams of copper sulphate are dissolved in 150 c.c. of water, 10 grams of anhydrous glycerine being added and then sodium hydroxide solution until the precipitate first formed is redissolved, excess of the alkali being avoided. The solution is kept in a tightly closed bottle in the dark.

Procedure.

1. Mixed wool and cotton fabric.

(*a*) Moisture : determined as on p. 455.

(*b*) Cotton. A piece of the fabric weighing 3–5 (*p*) grams is boiled for 15 minutes with 100 c.c. of the sodium carbonate solution, then washed well in running water and immersed in 100 c.c. of the boiling potassium hydroxide solution in a beaker which is left on a boiling water-bath for 20 minutes. The fabric is afterwards washed in running water, boiled for 15 minutes with 100 c.c. of distilled water, washed with alcohol and then with ether and finally dried in an oven at 100–105° and weighed.

The weight of the remaining fabric (*c*) represents the cotton in the fabric taken, so that $f_1 = \dfrac{100 \times c}{p}$.

(*c*) Wool. Another portion of about 3–5 grams of the fabric is weighed (*p*), boiled for 15 minutes with 100 c.c. of the sodium carbonate solution, washed with running water, immersed for 2 hours in the sulphuric acid in the cold, washed in running water, boiled for 15 minutes in distilled water, washed with alcohol and then with ether, dried at 100–105° in the ordinary way and weighed.

The weight of the remaining fabric (*l*) represents the wool in the fabric, so that $f_2 = \dfrac{100 \times l}{p}$.

(*d*) Dressing, colour and losses. These are obtained together by difference, the sum of the moisture, cotton and wool being subtracted from 100, i.e., $100 - (U + f_1 + f_2)$.

EXAMPLE :

(*a*) 5 grams of the fabric lose 0·385 gram at 100–105°. Percentage of moisture = 7·70.

(*b*) 5 grams of the fabric, when treated with potash, leave 2·541 grams of cotton. Percentage of cotton = 50·82.

(*c*) 5 grams of the fabric, after treatment with sulphuric acid, leave 1·824 grams of wool. Percentage of wool = 36·48. The composition of the fabric is thus :

(*a*) Moisture (*U*)	. . . . . .	7·70%
(*b*) Cotton (f_1)	. . . . . .	50·82
(*c*) Wool (f_2)	. . . . . .	36·48
(*d*) Dressing, colour and losses (*A*)	. . .	5·00
		100·00

The composition of the fabric in wool and cotton in the state in which they occur in the fabric is then obtained by successive application of the general formulæ I, II and IV ; thus :

$$a_1 = \frac{5 \times 50\cdot82}{100 - 7\cdot70 - 5} = 2\cdot91 \text{ (dressing of the cotton).}$$

$$a_2 = \frac{5 \times 36\cdot48}{100 - 7\cdot70 - 5} = 2\cdot09 \text{ (dressing of the wool).}$$

$$u_1 = \frac{7\cdot70 \times 50\cdot82 \times 8\cdot11}{50\cdot82 \times 8\cdot11 + 36\cdot48 \times 12\cdot36} = 3\cdot68 \text{ (moisture of the cotton).}$$

$$u_2 = \frac{7\cdot70 \times 36\cdot48 \times 12\cdot36}{50\cdot82 \times 8\cdot11 + 36\cdot48 \times 12\cdot36} = 4\cdot02 \text{ (moisture of the wool).}$$

$x_1 = 50\cdot82 + 2\cdot91 + 3\cdot68 = 57\cdot41$ (percentage of dressed, moist cotton).

$x_2 = 36\cdot48 + 2\cdot09 + 4\cdot02 = 42\cdot59$ (percentage of dressed, moist wool).

The same results are obtained directly by application of formulæ V.[1]
Thus the fabric may be regarded as composed of

Cotton yarn — 57·41%
Woollen yarn — 42·59%.

2. Mixed cotton and natural silk fabric.

(*a*) Estimation of the moisture : as on p. 455.

(*b*) Estimation of the cotton : as in 1 (*b*).[2]

(*c*) Estimation of the silk. A piece of the fabric weighing 3–5 grams (*p*) is boiled for 15 minutes with 100 c.c. of the sodium carbonate solution, and successively washed in running water, boiled for 15 minutes with distilled water, washed with alcohol and then with ether, dried at 100–105° and weighed. The fabric of weight *P* thus obtained is immersed for 1

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[1] If, as in this case, there are only two fibres, when the dressing, colour and moisture have been assigned to one of the two, the other—with its dressing and moisture —may be determined by difference.

[2] In this case the heating on the water-bath is prolonged to half an hour since, especially with fabrics containing either heavily weighted silk or wild (tussah) silk, the dissolution of this in potash takes place more slowly than with wool.

minute in 100 c.c. of boiling zinc chloride [1] and then washed successively with faintly acidified water, pure water, alcohol and ether, and dried at 100–105° and weighed (P').[2]

The percentage of silk in the fabric is given by :

$$\frac{(P - P') \times 100}{p}.$$

(d) *Dressing, colour, losses.* These are obtained together by difference :
$100 - (U + f_1 + f_2)$.

EXAMPLE :

(a) 4·820 grams of fabric lost 0·258 gram at 100–105°. Moisture = 5·35%.

(b) 5·243 grams of fabric, after treatment with potash, left 3·607 grams of cotton. Cotton = 68·80%.

(c) 4·620 grams of fabric, treated as in (c) (above), gave 0·602 gram of silk $(P - P')$. Silk = 13·03%.

The composition of the fabric is hence :

(a) Moisture (U)	.	.	.	.	.	.	5·35%
(b) Cotton (f_1)	.	.	.	.	.	.	68·80
(c) Silk (f_2)	.	.	.	.	.	.	13·03
(d) Dressing, colour, losses (A)	.	.	.	.		12·82
							100·00

To distribute the dressing, colour and moisture among the various fibres formulæ V may be applied directly. If x_1 and x_2 are the percentages of moist. dressed cotton and silk respectively, and the coefficients of normal moisture are introduced,[3] we have :

$$x_1 = \frac{68·80 \times 94·65}{81·83} + \frac{5·35 \times 68·80 \times 8·11}{68·80 \times 8·11 + 13·03 \times 9·29} = 83·97.$$

$$x_2 = \frac{13·03 \times 94·65}{81·83} + \frac{5·35 \times 13·03 \times 9·29}{68·80 \times 8·11 + 13·03 \times 9·29} = 16·03.$$

Thus, the fabric is composed of

Cotton .	.	.	.	.	.	.	83·97%
Silk	.	.	.	.	.	.	16·03

3. **Mixed woollen and natural silk fabric.**

(a) Estimation of the moisture : as on p. 455.

(b) Estimation of the wool : as in 1 (c).

(c) Estimation of the silk : as in 2 (c).

(d) Dressing, colour and losses : by difference, $100 - (U + f_1 + f_2)$.

EXAMPLE : *See* preceding case under 2. In assigning the moisture to the wool, the coefficient 12·36 is employed.

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[1] With weighted silk dyed black it is necessary to prolong the immersion to 1½ minute and with wild silk to 2–3 minutes. The zinc chloride may be replaced by Löwe's solution, in which the fabric is immersed completely for about 2–3 hours in the cold. A better plan consists in making two determinations, one with zinc chloride and the other with Löwe's solution.

[2] This weight P', referred to 100 parts of the fabric, represents the amount of cotton in the fabric and hence serves as a check on the preceding determination.

[3] For black weighted silk the coefficient 13·64 is used and for white or coloured weighted silk, 9·89.

4. Mixed cotton, wool and natural silk fabric.

(a) Estimation of the moisture : as on p. 455.

(b) Estimation of the cotton : as in 1 (b).[1]

(c) Estimation of the wool : as in 1 (c).

(d) Estimation of the silk : as in 2 (c).

(e) Dressing, colour and losses : by difference, $100 - (U + f_1 + f_2 + f_3)$.

EXAMPLE :

(a) 4·852 grams of fabric lose 0·408 gram at 100–105°. Moisture = 8·41%.

(b) 5·024 grams of fabric, after treatment with potash, leave 0·797 gram of cotton. Cotton = 15·86%.

(c) 4·808 grams of fabric, after treatment with sulphuric acid, leave 2·056 grams of wool. Wool = 42·76%.

(d) 5·260 grams of fabric, after the treatment described under 2 (c), give 0·608 gram of silk $(P - P')$. Silk = 11·56%.

The composition of the fabric is hence :

(a) Moisture (U)	8·41%
(b) Cotton (f_1)	15·86
(c) Wool (f_2)	42·76
(d) Silk (f_3)	11·56
(e) Dressing, colour, losses (A)	21·41
	100·00

The dressing and colour may be distributed to the different fibres and the corresponding amounts of moisture allotted to these by direct application of the general formulæ VI, where x_1, x_2 and x_3 represent respectively the percentages of cotton, wool and silk. The last may also be calculated by difference.

By means of the formulæ we obtain :

$$x_1 = \frac{15\cdot86 \times 91\cdot59}{70\cdot18} + \frac{8\cdot41 \times 15\cdot86 \times 8\cdot11}{15\cdot86 \times 8\cdot11 + 42\cdot76 \times 12\cdot36 + 11\cdot56 \times 9\cdot29} = 22\cdot11$$

$$x_2 = \frac{42\cdot76 \times 91\cdot59}{70\cdot18} + \frac{8\cdot41 \times 42\cdot76 \times 12\cdot36}{15\cdot86 \times 8\cdot11 + 42\cdot76 \times 12\cdot36 + 11\cdot56 \times 9\cdot29} = 61\cdot62$$

$$x_3 = \frac{11\cdot56 \times 91\cdot59}{70\cdot18} + \frac{8\cdot41 \times 11\cdot56 \times 9\cdot29}{15\cdot86 \times 8\cdot11 + 42\cdot76 \times 12\cdot36 + 11\cdot56 \times 9\cdot29} = 16\cdot27$$

5. Mixed fabric of cotton and artificial silk with a cellulose basis [2]:

(a) Estimation of the moisture : as on p. 455.

(b) Estimation of the cotton and artificial silk. The procedure described under 2 (c) is followed, care being taken to prolong the immersion in zinc chloride to 1½ minute ; the weight P' obtained represents the amount of cotton contained in the piece of fabric taken and the difference $(P - P')$, gives the quantity of artificial silk.

(c) Dressing, colour and losses : by difference, $100 - (U + f_1 + f_2)$.

The usual formulæ are employed to allot the dressing, colour and moisture to the various fibres, the coefficient of normal moisture being 11 for artificial nitrocellulose or viscose silks or 9·50 for cellulose silk.[3]

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[1] See note 2 on p. 466.

[2] Artificial silk in fabrics is usually determined by unravelling.

[3] See K. Süvern : *Die künstliche Seide*, Berlin, 1912, p. 583 ; Hassack : *Oester reichische Chemiker Zeitung*, 1900, p. 268.

6. Mixed fabric of wool and artificial silk with a cellulose basis.

(a) Determination of the moisture : as on p. 455.

(b) Determination of the wool : as in 1 (c).

(c) Determination of the artificial silk : as in 1 (b).

(d) Dressing, colour and losses : by difference, 100 $- (U + f_1 + f_2)$.

7. Mixed fabric of cotton, wool and artificial silk with a cellulose basis.

(a) Determination of the moisture : as on p. 455.

(b) Determination of the cotton. A piece of the fabric of weight p (3–5 grams) is boiled for 15 minutes with 100 c.c. of sodium carbonate, then washed well in running water and immersed in 100 c.c. of boiling potassium hydroxide solution in a glass beaker, which is left on a boiling water-bath for 20 minutes. The fabric is then washed well with running water, boiled for 15 minutes with 100 c.c. of distilled water, immersed for $1\frac{1}{2}$ minute in 100 c.c. of boiling zinc chloride, washed successively with slightly acidified water, pure water, alcohol and ether, dried at 100–105° and weighed.

The weight (c) thus obtained represents the cotton in the weight p of fabric used, so that the percentage of cotton is :

$$f_1 = \frac{c \times 100}{p}.$$

(c) Determination of the wool : as in 1 (c).

(d) Determination of the artificial silk : as in 2 (c), care being taken to prolong the immersion in zinc chloride to $1\frac{1}{2}$ minute.

(e) Dressing, colour and losses : by difference, 100 $- (U + f_1 + f_2 + f_3)$.

8. Mixed fabrics containing natural silk and artificial silk based on either cellulose, or nitrocellulose or viscose.

Where natural and artificial silks are present together, use is made of the property exhibited by 10% caustic potash solution and by Löwe's solution, in the conditions already mentioned, of dissolving natural silk and leaving artificial silk undissolved.

A. Mixed fabric containing cotton, wool, natural silk and artificial cellulose, nitrocellulose or viscose silk.

(a) Estimation of the moisture : as on p. 455.

(b) Estimation of the cotton : as in 7 (b).

(c) Estimation of the wool : as in 1 (c).

(d) Estimation of the natural silk : with Löwe's liquid, as in 2 (c).

(e) Estimation of the artificial silk. The natural and artificial silks together are estimated as in 2 (c), care being taken to prolong the immersion in zinc chloride solution to $1\frac{1}{2}$ minute, or in the case of wild silk to 2–3 minutes. Subtraction from the amount thus found of the weight of natural silk determined by means of Löwe's solution gives the quantity of artificial silk present in the piece of fabric taken.

(f) Dressing, colour and losses : by difference, 100 $- (U + f_1 + f_2 + f_3 + f_4)$.

B. With other types of mixed fabrics containing natural silk and artificial silk an analogous method is followed, attention being paid to the indications given in the preceding paragraphs.

6. Quantitative Determination of a Single Fibre in a Fabric.—

In some cases, for instance, when only a small quantity of material is available, the determinations may be restricted to only one fibre in a fabric of two kinds of fibre or to two fibres in a fabric of three textile materials. In such cases direct determinations must be made of the moisture and of the dressing and colouring matter, proportionate parts of these being assigned to the fibre determined. The results thus obtained do not possess the accuracy of those furnished by the methods described above, but in some cases they suffice.

The moisture is determined as on p. 455.

The dressing and colour are determined as on p. 458. With lightly dressed fabrics, however, the treatment with 3% hydrochloric acid may be omitted, only that with 0·1% sodium carbonate being employed. The hydrochloric acid treatment should always be omitted with fabrics containing silk.

If this shortened method is employed, the following rules must be followed : in cotton and wool fabrics, the cotton is determined for preference as in case 1 (b) and the wool calculated by difference. In cotton and silk or wool and silk fabrics, the silk is determined for preference in the manner described in case 2 (c) and the other component calculated by difference. In cotton, wool and natural silk fabrics, the silk (2, c) and cotton (1, b) are determined for preference and the wool calculated.

Also, where only one piece of fabric (weighing about 5 grams) is available, all the different determinations may be made on it in succession : (1) moisture, (2) dressing and colour, (3) cotton (in the case of cotton and wool), or silk (with cotton and silk or wool and silk), or silk and cotton (in fabrics of cotton, wool and silk).

EXAMPLES :

I. Cotton and wool fabric.

(a) 4·500 grams of the fabric, when dried at 100–105°, lost 0·460 gram. Moisture = 10·22%.

(b) The remaining fabric, after treatment with sodium carbonate, etc., lost 0·212 gram. Dressing and colour = 4·71%.

(c) The fabric from (b), after treatment with potash, left 2·428 grams of cotton. Cotton = 53·95%.

(d) Wool by difference = 31·12%.

Hence the composition of the fabric is :

(a) Moisture (U)	10·22%
(b) Dressing and colour (A) . . .	4·71
(c) Cotton (f_1)	53·95
(d) Wool (f_2)	31·12
	100·00

The usual formulæ V may be applied as in the preceding examples :

$$x_1 = \frac{53·95 \times 89·78}{85·07} + \frac{10·22 \times 53·95 \times 8·11}{53·95 \times 8·11 + 31·12 \times 12·36} = 62·37$$

$$x_2 = \frac{31·12 \times 89·78}{85·07} + \frac{10·22 \times 31·12 \times 12·36}{53·95 \times 8·11 + 31·12 \times 12·36} = 37·63$$

Thus, the fabric contains 62·37% of cotton and 37·63% of wool.

II. Cotton, wool and silk fabric.

(a) 5·240 grams of the fabric, dried at 100–105°, lost 0·422 gram. Moisture = 8·05%.

(b) The fabric from (a), when treated with sodium carbonate, etc., lost 0·538 gram. Dressing and colour = 10·27%.

(c) The fabric from the preceding operation, loses 0·600 gram in zinc chloride. Silk = 11·45%.

(d) The residual fabric leaves 1·200 gram of cotton after treatment with potash. Cotton = 22·90%.

(e) The wool by difference = 47·33%.

Thus, the composition of the fabric is :

(a) Moisture (U)	. . . . . .	8·05%
(b) Dressing and colour (A)	. . . .	10·27
(c) Silk (f_3)	. . . . . .	11·45
(d) Cotton (f_1)	. . . . . .	22·90
(e) Wool (f_2)	. . . . . .	47·33
		100·00

Indicating the percentages of cotton, wool and silk by x_1, x_2 and x_3 respectively, the general formulæ VI give, as in the example of case 4 (*see* p. 467) :

$$x_1 = \frac{22 \cdot 90 \times 91 \cdot 95}{81 \cdot 68} + \frac{8 \cdot 05 \times 22 \cdot 90 \times 8 \cdot 11}{22 \cdot 90 \times 8 \cdot 11 + 47 \cdot 33 \times 12 \cdot 36 + 11 \cdot 45 \times 9 \cdot 29} = 27 \cdot 48$$

$$x_2 = \frac{47 \cdot 33 \times 91 \cdot 95}{81 \cdot 68} + \frac{8 \cdot 05 \times 47 \cdot 33 \times 12 \cdot 36}{22 \cdot 90 \times 8 \cdot 11 + 47 \cdot 33 \times 12 \cdot 36 + 11 \cdot 45 \times 9 \cdot 29} = 58 \cdot 65$$

$$x_3 = \frac{11 \cdot 45 \times 91 \cdot 95}{81 \cdot 68} + \frac{8 \cdot 05 \times 11 \cdot 45 \times 9 \cdot 29}{22 \cdot 90 \times 8 \cdot 11 + 47 \cdot 33 \times 12 \cdot 36 + 11 \cdot 45 \times 9 \cdot 29} = 13 \cdot 87$$

Hence the fabric contains :

27·48% of cotton, 58·65% of wool and 13·87% of silk.

7. Investigation of the Nature of the Colour.

—This may be carried out by A. G. Green's method,[1] which is based on :

(a) Extraction of the colouring matter, the group to which it belongs (basic, acid, saline or direct or substantive, mordant, vat, etc.) being determined.

In this connection it must be borne in mind that in some of these extraction tests on naturally coloured and raw cotton, flax, wool, hair, etc., an appreciable quantity of yellowish-brown colouring matter is removed, and that raw silks of a natural yellow or green colour exhibit special behaviour if subjected to some of these tests, e.g., to treatment with concentrated acids.[2]

(b) Tests of reduction (with sodium hydrosulphite) and of reoxidation (by the air or potassium persulphate), which indicate to which group the colouring matter belongs as regards its chemical composition or its chromophore, as shown in the following scheme :

[1] A. G. Green, H. Yeoman, J. R. Jones, F. G. C. Stephens and G. A. Haley, *Journ. Soc. Dyers and Colourists*, 1905, XXI, pp. 236 *et seq.*; 1907, XXIII, pp. 252 *et seq.*, and A. G. Green, *The Analysis of Dyestuffs*, 1916, pp. 55 *et seq.*

[2] See A. Cappelli : Behaviour to tintorial analysis of naturally coloured animal and vegetable fibres : *Ann. Labor. Chim. centrale Gabelle*, Vol. VII, p. 213.

The Fibre is decolorised by hydrosulphite.			The colour of the fibre is not altered by hydrosulphite.	The colour of the fibre is not destroyed but changed by hydrosulphite, the original colour reappearing in the air or with persulphate.
The colour reappears in the air.	The colour reappears, not in the air but with persulphate.	The colour reappears neither in the air nor with persulphate.		
Azine, oxazine, thiazine and indigoid groups	Triphenyl-methane group	Nitro-, nitroso- and azo-colouring matters.	Pyrone, acridine, quinoline, and thiazole groups. Some members of the anthracene group.	Many colours of the anthracene group.

In some cases a further subdivision of the groups is effected by other reactions (e.g., with concentrated sulphuric or hydrochloric acid, or with caustic soda).

For the following colours : yellow and orange, red, purple and violet, blue green, brown, black and grey, the various groups of colouring matters are arranged in tables (*see* pp. 477 *et seq.*). In some cases investigation should be made also in the tables relating to colours similar to that of the sample or in those relating to colours which when mixed may give the colour of the sample.

For each group and sub-group only some of the typical colouring matters are indicated.

If, when the group has been fixed, it is desired to identify also the colouring matter, the latter is sought among those belonging to the group capable of giving colours like that of the sample, use being made of their characteristic reactions.[1]

As confirmation of the results obtained it will be well to compare the tint and reactions of the fabric with those of a sample dyed with the colouring matter and in the manner indicated by the results of the tests.

Green's method includes two series of tables, one for colouring matters fixed on wool and the other for those fixed on cotton. The former series may serve also for the examination of dyestuffs on silk and the latter for those on the other principal vegetable fibres, excepting that small variations are necessary in both cases for certain groups of colouring matters.

(*a*) COLOURING MATTERS ON WOOL.

Reagents. 1. 5% acetic acid (5 c.c. of glacial acetic acid and 95 c.c. of water).

2. 1% ammonia (1 c.c. of ammonia $D = 0.884$ in 100 c.c. of water).

3. 1% aqueous-alcoholic ammonia (1 c.c. of ammonia $D = 0.884$, 50 c.c. of 95% alcohol and 50 c.c. of water).

4. Dilute alcohol (equal volumes of 95% alcohol and water).

5. 1 : 10 hydrochloric acid (10 c.c. of hydrochloric acid $D = 1.152$, i.e., about 30%, in 100 c.c. of water).

6. 10% aqueous sodium hydroxide.

7. 5% crystallised sodium acetate solution.

[1] *See* note, p. 424.

8. Cold saturated aqueous potassium per sulphate solution or 1% aqueous ammonium persulphate.[1]

9. Hydrosulphite B : 50 grams of hydrosulphite N F conc. or of hyraldite C extra or of rongalite C are dissolved in 500 c.c. of water and the solution then acidified with 2 c.c. of acetic acid.

10. Hydrosulphite A X : 50 grams of hydrosulphite N F conc. or of rongalite C are dissolved in 150 c.c. of hot water, 0·25 gram of precipitated (not sublimed) anthraquinone, reduced to the form of a fine paste with a little of the solution, being added to the rest of the solution at 80–90°, and the volume then made up to 500 c.c. with cold water. This reagent should always be slightly alkaline to litmus paper ; in time it turns acid.

Procedure. The sample is treated first with cold water and then with boiling water in order to ascertain if it contains any unfixed colouring matter or any dressing substances ; any such should be removed before the systematic investigation is begun. The following preliminary test for metallic mordants should also be made immediately : A small piece of the sample is burnt in a flame, the colour and behaviour on heating of any ash remaining being observed : in presence of an aluminium mordant, the ash is white and becomes incandescent when heated ; with a tin mordant, the ash is white and becomes incandescent and yellowish when heated ; in presence of a chromium mordant, the ash is greenish, and in presence of an iron mordant, reddish-brown.

It should, however, be borne in mind that in some cases the ash does not depend on the nature of the dyeing to which the sample has been subjected : thus, for example, the presence of chromium or iron is sometimes due to the use of shoddy in the manufacture of a woollen cloth, while the presence of tin in the ash of a silken fabric may be caused by the weighting.

The sample is then tested in the manner and in the order indicated in the tables on pp. 477 *et seq.*, attention being paid to the following points :

1. The reactions are carried out in test-tubes or, better, in porcelain dishes, pieces of fabric about 2–3 cm. square being generally used and covered with the reagent.

If the fabric consists of yarns of different colours and characters, each type should be separated and examined alone.

Excepting where expressly stated otherwise, each successive test should be made on a fresh piece of the sample.

To decide if a given treatment results in the removal (" stripping ") of much colour, the sole criterion should not be the coloration assumed by the reagent used, it being necessary to compare also the colours of the sample before and after treatment.

2. In the tests with dilute acetic acid or dilute ammonia, the extraction should be repeated on the same piece of fabric with the view of completing the extraction and also because it sometimes happens that, in the first boiling with dilute ammonia, certain acid dyestuffs dye white cotton, whilst during the second boiling such coloration assumed by the cotton in the first treatment disappears. When boiling with white cotton is prescribed, a

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[1] If the persulphate solutions are alkaline, they should be carefully neutralised with a dilute acid.

small piece of mercerised white cotton material is used (about one-third as large as the sample used). If the colour of the fabric is not very intense, more of the sample is used and less of the cotton.

To render certain acid colours more stable to light, copper salts are sometimes used in the dye bath ; in such cases it is well, before testing for the colouring matter, to remove the copper from the sample by boiling it with oxalic acid solution.

3. In the sodium acetate test the cotton remains coloured after about a minute with a saline colouring matter and after about two minutes in the case of dyes on saline mordants.

With reference to acid and saline colouring matters, there is sometimes a certain difficulty in deciding if the dyeing was effected with one or the other. Indeed, some saline colouring matters, such as the sulpho-colouring matters, colour white cotton very little, even if boiled for a long time with 1% ammonia or 5% sodium acetate solution, whilst some few acid colouring matters (such as solid red A and wool red B) dye white cotton when boiled with 1% ammonia. Further, the case with which acid colouring matters are removed by means of 1% ammonia is very variable, some being faded easily and abundantly, and others, among them certain types of patented blues, only with difficulty.

4. In the reduction tests a piece of the fabric is boiled for from fifteen seconds to a minute with hydrosulphite, then well washed under a water-tap, squeezed and left on a white paper. Reoxidation in the air usually takes place immediately, but sometimes slowly, and in the latter case it may be accelerated by exposure to ammonia vapour. If the colour does not reappear within an hour, the effect of persulphate is tried. To this end the piece of decolorised fabric is boiled with water and the persulphate added drop by drop, excess being avoided. The colour reappears sometimes with the original intensity, but sometimes less strongly, in consequence of the greater or less solubility of the leuco-derivative ; with safranine and its azo-derivatives it reappears as violet owing to combination of the leuco-safranine with the formaldehyde of the reagent.

5. The test for the indigoid colouring matters is carried out in the following manner : A piece of the sample is boiled for 1–2 minutes with recently distilled aniline ; if the liquid remains colourless it is evaporated carefully to dryness. The dry residue thus obtained after expulsion of all the aniline is cautiously heated over a small flame : the presence of an indigoid colouring matter is indicated by the production of coloured vapours. To differentiate the colouring matters of the indigoid class, as for instance indigo and ciba blue, Holden [1] recommends the use of the colour of the chloroform extract.

6. As a confirmatory test for triphenylmethane colouring matters, use may be made of the fact that many of these become pale yellow or yellowish-brown when the fibre is treated with concentrated sulphuric acid.

7. For the detection of the principal mordants the following method may be employed : About 10 grams of the fabric are incinerated in a platinum dish and the ash then fused with about five times its weight of dry sodium-potassium carbonate and a little potassium nitrate.

[1] *Journ. Soc. Dyers and Colourists*, 1909, p. 47.

A yellow coloration of the fused mass indicates chromium. The mass is taken up in the platinum dish with water and acetic acid then added a little at a time until the reaction is acid. In a small portion of the acetic acid solution the presence of chromium may be confirmed by means of lead acetate. The acetic acid solution and any undissolved part of the mass are concentrated to a small volume in a porcelain dish over a naked flame and then taken to dryness on a water-bath. The residue is heated for some time in an air-oven at 110° and then treated with water and hydrochloric acid and filtered. The filtrate is tested for tin and copper by means of hydrogen sulphide.

Any precipitated sulphides being removed by filtration, the filtrate is boiled to expel hydrogen sulphide, then oxidised with a few drops of concentrated nitric acid and boiled with ammonium chloride and ammonia. The liquid is then filtered and the precipitate carefully washed with hot water and dissolved in dilute nitric acid, the nitric acid solution being treated with excess of sodium hydroxide, boiled for a few minutes and filtered when cold. Any ferric and chromium hydroxides remain on the filter, the filtrate containing the alumina as sodium aluminate. If the filtrate is heated to boiling with ammonium chloride, an abundant precipitation of gelatinous white flocks will occur in the case of a sample dyed on an aluminium mordant.

With reference to the detection of mordants, the following should be borne in mind :

(a) The colour and appearance of the ash may sometimes be important factors in deciding if a mordant has been used. The ash is white in the case of mordanting with aluminium or tin salts, greenish with a chromium mordant, and brick-red with an iron mordant, and in any case when a mordant has been used, the ash appears heavy.

(b) With products in the manufacture of which shoddy has been employed, ash of various colours may be obtained according to the mordant used in dyeing the original material from which the shoddy was obtained.

(c) Wool naturally contains small quantities of iron and aluminium, which are detected as hydroxides when the ash is analysed exactly as described above. Woollen goods dyed with an iron or aluminium mordant give, in comparison with those of undyed wool, a more abundant and heavier ash, which is reddish-brown when a ferric salt has been used ; the precipitates of the hydroxides are also more distinct and abundant.

(d) With goods mordanted by means of tin salts it may happen that, in the disaggregation of the ash, the platinum dish is attacked slightly. This inconvenience may be obviated by following the method given in the foot-note,[1] which however requires about a gram of ash and much time.

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[1] With dyed goods in which the presence of tin mordant is suspected, the following procedure may be followed : About 40 grams of the material are incinerated and the ash, mixed with water in a conical flask, treated with a volume of zinc dust about one-half of that of the ash, together with a few drops of dilute sulphuric acid. The liquid is mixed and heated on a water-bath, a few drops of sulphuric acid being added occasionally and the flask shaken until all the zinc is dissolved. Under these conditions the tin passes into the metallic state. The liquid is then filtered and the undissolved part washed on the filter with hot water, the filtrate and wash water being retained (a). The undissolved matter is treated in a test-tube with concentrated hydrochloric acid and when all action has ceased, the liquid is decanted off and filtered if necessary, the residue being washed carefully on the filter, first with water acidified with hydrochloric acid and then with distilled water. The mixture of the hydrochloric acid solution and wash waters is kept (b). The residue from the treatment with concentrated hydrochloric acid, if of appreciable amount, is dried in a platinum dish on a water-bath

(e) In the dyeing of certain woollen goods, very small quantities of copper salts are sometimes used, and in these cases the identification of copper in the ash may present some difficulty.

(f) In certain cases only analysis of the ash shows if the colour of a sample is natural or artificial, and in the latter case the mode of dyeing may also be indicated. This is the case, for instance, with fur dyed with the help of lead or bismuth sulphide.

8. The determination of the colouring matters constituting the mixtures used to obtain a given colour is usually a complex problem which varies from one case to another and can be solved only by one possessing an exact knowledge of the analytical method and of the various processes of dyeing.

In such investigations the following should be borne in mind :

(a) If a mixture is composed of two or more colouring matters belonging to the same chemical group, it behaves like a single colouring matter. In certain cases such differences may be observed, with reference to the solubility and the greater or less resistance towards reagents of the separate components, as allow the latter to be characterised. Thus, a green consisting of an acid azo yellow and an acid azo blue may be recognised by the hydrosulphite test ; the blue will usually be reduced first and the colour will change from green to yellow and then be destroyed completely. The original colour, being due to two azo-colouring matters, is restored neither by the air nor by persulphate. Moreover, on treatment with ammonia, the yellow is usually removed first and may be fixed on white wool and then identified.

(b) Mixtures of colouring matters of different groups are generally more easy to detect. For instance, a sea blue obtained with a patent blue and an azo-orange will, when reduced with hydrosulphite, give a bright blue before becoming decolorised. On subsequent oxidation with persulphate the colour of the patent blue will reappear.

(c) Where a mixture of colouring matters of the azine, oxazine, thiazine and triphenylmethane groups has been used, the first three—after the reduction test—will reappear on simple exposure to the air and the last only when treated with persulphate.

(d) In some cases total or partial separation of the colouring matters constituting a mixture may be effected by fractional extraction with alcohol or with dilute acetic acid. When the different colouring matters are separated in this way, each of them can be fixed on white wool or silk and then identified. Before this transference of the colouring matter to wool or silk is effected, the alcohol should be expelled by boiling or the acetic acid neutralised.

(e) In certain cases the colouring matters constituting a given mixture may be separated by means of suitable solvents. Thus, for instance, a

and then fused with sodium and potassium carbonates. The mass is treated with water and dilute acetic acid and evaporated to dryness on a water-bath, the residue being taken up in dilute hydrochloric acid. This acid solution, together with liquids (a) and (b) is evaporated to dryness in a porcelain dish on a water-bath and the residue kept for some time at 110°. The residue is then taken up in dilute hydrochloric acid and the procedure indicated above followed for the detection of tin and other mordants, especially aluminium, salts of which are sometimes added to the tin salts used in the dyeing of woollen goods.

mixture of a mordant colouring matter fixed by means of chromium and an ordinary acid colouring matter may be identified by extracting in a suitable apparatus with pyridine, which removes the acid colouring matter, whereas the mordant colouring matter remains totally fixed on the fibre and may hence be identified. The pyridine is distilled off and the acid colouring matter in the residue then fixed on wool and identified by means of the corresponding table.

(f) To separate indigo and other vat colouring matters from mordant and acid colouring matters the following procedure may be followed: In an ordinary extractor connected with an air condenser is placed a piece of the sample previously dried in an oven, this being covered with a layer of wool and a thermometer arranged with its bulb in contact with the sample. Extraction is carried out with a mixture of 100 parts of cresol (commercial 97–98% cresylic acid) and 30 parts of "solvent naphtha" (crude xylole) having the b.pt. 125–140°, or with a mixture of 75 parts of cresol with 25 parts of heavy petroleum benzine of b.pt. 155–170°. By this means the temperature of the extractive liquid in contact with the sample is about 100–105° and should not exceed 110°. This treatment results in the extraction of the vat colouring matters, whilst most of the acid and mordant colouring matters remain on the fibre and may then be identified.

(g) Logwood colours are separated from acid, mordant and vat colouring matters by boiling with dilute hydrochloric acid, which usually takes up only the logwood giving a crimson extract.

Red-wood and other dye-woods generally behave like logwood. Acid alizarin reds are also extracted.

(h) With "vatted blacks" (mixtures of indigo and logwood) the indigo alone is extracted by the above cresol or pyridine mixture, or the logwood alone by boiling dilute hydrochloric acid.

(i) If an acid black is present in addition to the indigo and logwood, the logwood is first extracted with dilute hydrochloric acid, the indigo being then removed by the above cresol mixture, so that only the acid colouring matter afterwards remains on the fibre.

TABLES

For the Identification of Artificial Colouring Matters on Wool

TABLE LIV

Yellow and Orange   Colo

Boil twice for one minute with   5 per c

Much colour is stripped : **Basic Dyestuff.** Boil with Hydrosulphite A X or B.					Little or no colour is stripped : **Acid, Vat, Mordant, or Salt**					Dyestu
Not decolorised, or only slightly altered. Treat fibre with cold conc. sulphuric acid.				Decolorised. Colour is not restored either by air or by persulphate : *Azo Class.*	Much colour is stripped, but cotton remains white : **Acid Dyestuff.** Boil with Hydrosulphite A X or B.					or onl
Green fluorescent solution : *Acridine Class.*	Colourless solution : *Ketonimide* and *Thiazol Class.* Boil fibre with dilute hydrochloric acid (1 : 10).					Decolorised. Colour is not restored either by air or by persulphate : *Azo* or *Nitro Class.* Add excess of conc. hydrochloric acid to the ammoniacal extract.				More pres *Fla* o *Ke Cl*
	Fibre and solution colourless.	Fibre and solution pale yellow.	Fibre and solution orange.		Colour unaffected : *Quinoline* or *Pyrone Class.*	Colour unaffected.	Solution becomes colourless or very pale yellow.	Solution becomes red or orange-red.	Solution becomes violet or violet-red.	
1	2	3	4	5	6	7	8	9	10	
Phosphine, benzoflavine, coriphosphine, rheonine, patent phosphine, acridine orange, acridine yellow, flavophosphine, aurophosphine, diamond phosphine, brilliant phosphine, etc.	Auramine.	Thioflavine T, methylene yellow H, rhoduline yellow.	Rhoduline orange N.	Chrysoidine, tannin orange, Janus yellow, azo phosphine, new phosphine, etc.	Quinoline yellow, quinaldine yellow, uranine, eosine orange, etc. Also turmeric.	Orange G, 2 G, G T, R, etc. Croceine orange, tartrazine, flavazine, hydrazine yellow, fast light yellow and orange, fast wool yellow, wool fast orange, Guinea fast yellow, xylene yellow and light yellow, tartraphenine, kitone yellow, supramine yellow, fast acid orange R H, etc.	Naphthol yellow S, Martius yellow, naphthylamine yellow, naphthalene yellow, citronine A, etc.	Indian yellow, fast yellow, azo flavine, brilliant yellow S, curcumine, orange II, etc. palatine light yellow, wool fast yellow, azo acid yellow, azo yellow, etc.	Metanil yellow, Victoria yellow, orange IV, orange M N, M N O, N, etc.	

General.—In the case of yellow and orange colours the indications are sharper when reduction is effected with hydrosulphite the decolorisation of the dyestuffs of other groups may be somewhat obscured by the yellow tint given by the anthraquinone, cence to the acetic acid extract. *Div. 6.*—Turmeric becomes much browner on boiling with dilute ammonia or sodium acetate. orange coloration (nitroamido compound). *Div. 11.*—Weld on Al is partially stripped by acetic acid, giving a colourless extract; tion. *Div. 17.*—Sulphone yellow and sulphone orange give only a comparatively slight stain on cotton after boiling two minutes

B. esp *Di* on wit

LIV

Colours on Wool

5 per cent. acetic acid.

Dyestuff. Boil twice for one minute with dilute ammonia (1 : 100) and a piece of white cotton. Keep the ammoniacal extract.

Little or no colour is stripped : **Vat, Mordant,** or **Salt Dyestuff.** Boil with Hydrosulphite A X or B.

Colour unaffected, or only slightly changed in shade. Test for a mordant.		Decolorised. Colour returns on exposure to air, or more quickly on oxidation with persulphate. Boil with 5 per cent. sodium acetate and a piece of white cotton for two minutes.		Decolorised. Colour is not restored either by air or by persulphate : *Azo Class.* Test for a mordant (Cr).				Colour changed to yellow-brown or brown : *Alizarine Class.* A mordant is present.
				Mordant present. Boil with 5 per cent. sodium acetate and a piece of white cotton for two minutes.		Mordant absent : *Azo Salt Dyestuff.* Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton. Stained.		
Mordant present : *Flavone* or *Ketone Class.*	Mordant absent : *Thiazol Salt Dyestuff.* Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton. The latter is stained.	Cotton remains white : *Indigoid Vat Dyestuff.* Confirm by extraction with aniline and sublimation test.	Cotton is stained : *Salt Dyestuff, Stilbene Class.*	Cotton remains white : *Acid-mordant Dyestuff.*	Cotton is stained : *Salt-mordant Dyestuff.*			
11	12	13	14	15	16	17		18
Fustic, quercitron bark, weld, flavine, alizarine yellow A and C, galloflavine, etc.	Thioflavine S, diamine fast yellow B, F F, M, sulphine, primuline, chloramine yellow, brilliant pure yellow, chorazol fast yellow, thiazol yellow Clayton yellow, chlorophenine, dianil pure yellow H S, naphthamine pure yellow G, diphenyl fast yellow, triazol fast yellow, Columbia yellow, oxydianil yellow, oxydiamine yellow, mimosa yellow, etc.	Helindone yellow and orange, ciba yellow and orange, ciba indigo yellow 3 G, thioindigo yellow and orange, etc.	Curcumine S, Mikado yellow, golden yellow and orange, direct yellow, stilbene yellow, diamine fast yellow A, A R, diamine orange D, dianil direct yellow S, chloramine orange, naphthamine yellow, diphenyl chrysoine, diphenyl citronine, sun yellow, polar yellow, polyphenol yellow, etc.	Acid alizarine yellow, eriochrome yellow, eriochrome phosphine, alizarine yellow G, 2 G, 3 G, R, flavazol, diamond flavine, anthracene yellow, alizadine yellow, chrome fast yellow, fast mordant yellow, salicine yellow D, diamond yellow, chrome yellow, chrome orange, etc.	Autochrome orange, mercerol yellow 2 R, mercerol orange 2 R, salicine orange G, salicine yellow G, metachrome yellow, etc.	Chrysophenine, chrysamine, diamine fast yellow 3 G, diamine yellow N, benzo fast yellow and orange, Congo orange, cotton yellow, carbazol yellow, Pluto orange, cresotine yellow, pyramine orange, toluylene yellow and orange, orange T A, hessian yellow, dianil orange, triazol yellow G, sulphon yellow and orange, etc.		Alizarine red S, etc., on Sn, alizarine orange S W on Cr, Al, Sn.

B. With hydrosulphite A X many of the dyestuffs of the thiazol group become considerably lighter, whilst, on the other hand, especially if the pattern is not thoroughly washed. *Div.* 1.—The acridine dyestuffs give a more or less pronounced green fluores-
Div. 8.—Nitro dyestuffs may be distinguished from azo by the production with hydrosulphite, prior to decolorisation, of a reddish-
on Cr or Sn it is not affected. *Div.* 15. Alizarine Yellow R and R W stain cotton slightly on boiling with sodium acetate solu-
with sodium acetate. The toluylene oranges are only reduced by hydrosulphite with great difficulty.

TABLE

Red Colours

Boil twice for one minute with

Much colour is stripped : Basic Dyestuff or Soluble Red Wood. Boil twice for one minute with dilute acohol (1 : 1).						Little or no colour is stripped : Acid, Vat, Mordant, or Salt					
Much colour is stripped : **Basic Dyestuff.** Boil with Hydrosulphite A X.						Much colour is stripped, but cotton remains white : **Acid Dyestuff.** Boil with Hydrosulphite A X.					
Colour unaffected : *Pyrone Class.*	Decolorised. Colour returns on exposure to air. Treat original fibre with cold conc. sulphuric acid.		Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenylmethane Class.*	Decolorised. Colour is not restored either by air or by persulphate : *Azo Class.*	Unaffected. Al or Cr is present in ash. On boiling with dilute ammonia the colour becomes much bluer.	Colour unaffected : *Pyrone Class.* On acidifying the ammoniacal extract, fluorescence is not discharged.	Decolorised. Colour returns on exposure to air : *Azine Class.*	Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenylmethane Class.*	Decolorised. Colour is not restored either by air or by persulphate : *Azo Class.* Boil with dilute bichromate.		Colour is changed to bright yellow, which slowly returns in air to original shade : *Anthraquinone Class.*
	Fibre and solution green : *Azine Class.*	Fibre and solution violet.							Colour unaffected.	Colour changed to dark maroon or blue-violet.	
1	2	3	4	5	6	7	8	9	10	11	12
Rhodamines, irisamine, anisoline, rosazeine, rhoduline pink, etc.	Safranine, induline scarlet, rhoduline red, diazine red, brilliant rhoduline red, brilliant rhoduline violet R, brilliant safranine, etc.	Cudbear, archil.	Magenta, fuchsine, diamond magenta, new magenta, cerise, etc.	Janus red.	Soluble red woods, e.g., Brazil wood, Lima wood, sapanwood, peachwood, etc.	An acid eosine or acid rhodamine, e.g., fast acid eosine, fast acid phloxine, acid rhodamine, acid rosamine, xylene red, brilliant kitone red, sulpho rosazeine, etc.	Rosinduline, azo carmine.	Acid magenta, acid fuchsine, fast acid red A.	Palatine scarlet, xylidine ponceau, Victoria scarlet, lanafuchsine, sorbine red, Biebrich acid red, crystal scarlet, fast red, croceine scarlet, Biebrich scarlet, wool and cloth reds, wool scarlet, acetyl red, amido naphthol red, eriocarmine, eriorubine, azo acid red, Guinea fast red, fast acid cochineal, etc.	Chromotrope, azofuchsine.	Alizarine rubinol.

Div. 2.—Induline scarlet gives a claret-red colour with concentrated sulphuric acid, which becomes green on addition of a tra which is reconverted into the red on boiling with ammonia. *Div.* 9.—Fast acid red A, although a *pyrone* derivative, also f LVI. *Div.* 10.—Fast red A and wool red B stain cotton on boiling with dilute ammonia. The group of acid azo colours may blue, or green). *Div.* 12.—Alizarine geranol B exhibits an exceptional behaviour, being reduced by hydrosulphite A X to a p "vat" dyes show a yellow fluorescence in chloroform solution. *Div.* 17.—Several of the red azo "mordant" dyestuffs, wh red B, acid alizarine red G, acid alizarine garnet R, omega chrome red B, and diamond red G.

LV

on Wool

5 per cent. acetic acid.

Dyestuff. Boil twice for one minute with dilute ammonia (1 : 100) and a piece of white cotton.

Part of the colour is stripped, and the wool becomes bluer. Boil with Hydrosulphite A X.		Little or no colour is stripped : **Vat**, **Mordant**, or **Salt Dyestuff**. Boil with Hydrosulphite A X.					
				Decolorised. Colour is not restored either by air or by perulphate : *A 10 Class.* Test for a mordant (Cr).			Colour slowly changed to orange or orange-brown. Original colour is restored by per-sulphate. A mordant is present. *Alizarine Class.*
Colour unaffected : *Pyrone Class.* The ammoniacal extract is fluorescent, and on acidifying, the fluorescence is discharged.	Colour is changed to yellow. Original colour is not restored on exposure to air, Sn is present.	Decolorised. Colour returns on exposure to air : *Indigoid Vat Dyestuff.* Confirm by extraction with aniline and sublimation test.	Decolorised. Colour does not return on exposure to air, but is restored by per-sulphate. A mordant is present (Al or Cr).	Mordant present. Boil with 5 per cent. sodium acetate and a small piece of white cotton for two or three minutes.		Mordant absent : *Salt Dyestuff.* Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton.	
				Cotton remains white : *Acid-mordant Dyestuff.*	Cotton is stained : *Salt-mordant Dyestuff.*		
13	14	15	16	17	18	19	20
Eeosine, eosine scarlet, phloxine, erythrosine, rose bengale, etc.	Cochineal scarlet.	Helindone red, scarlet, fast scarlet and pink, ciba red and scarlet, thioindigo red, thioindigo scarlet, vat red, etc.	Insoluble red woods, e.g., barwood, camwood.	Anthracene chrome red, acid alizarine red, eriochrome red, eriochrome bordeaux, eriochrome garnet oxychrome garnet, diamond red, palatine chrome red, omega chrome red, etc.	Anthracene red, acid anthracene red, autochrome red, salicine red, chrome fast red, etc.	Diamine, benzo, dianil, chlorazol, naphthamine, etc., reds, scarlets, and fast scarlets, erika, geranine benzopurpurine, milling reds and scarlets, polar red, etc.	Alizarine red W, I W S, S, S B, P S, etc., erweco alizarine acid red S B.

of water. Safranine, after reduction and oxidation, does not return to its original shade, but to a violet (methylene derivative), into this division. It reduces more slowly than the triphenylmethane dyestuffs and is similar to the fast acid violets of Table split up into classes by treatment of the fibre with concentrated sulphuric acid, when various colours are obtained (red, violet, yellow, which is permanent in air but changed on boiling with persulphate to a pale violet-brown. *Div.* 15.—Many of the red should fall into this group, are, when fixed upon wool, extremely difficult to reduce. This is especially the case with eriochrome

A.C. II.

31

Purple and Violet

Boil twice for one minute

Much colour is stripped : **Basic Dyestuff** or **Soluble Red Wood.** Boil twice for one minute with dilute alcohol (1 : 1).				[Little or no colour is stripped : **Acid, Vat, Mordant, or Salt**				
Much colour is stripped : **Basic Dyestuff.** Boil with Hydrosulphite A X.		Unaffected. Al or Cr is present in ash. On boiling with dilute ammonia, the colour becomes much bluer.	De-colorised. Colour returns on exposure to air : *Azine, Oxazine,* or *Thiazine Class.*	Much colour is stripped, but cotton remains white : **Acid Dyestuff.** Boil with Hydrosulphite A X.				Decolorised. Colour is not restored either by air or by persulphate : *Azo Class.*
				Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenylmethane* and *Pyrone Classes.* Boil with 5 per cent. sodium acetate for one minute.				
Decolorised. Colour returns on exposure to air : *Azine, Oxazine,* or *Thiazine Class.*	De-colorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenylmethane Class.*			Much colour is stripped, but solution remains colourless. Treat original fibre with cold conc. sulphuric acid.		Little colour is stripped. Spot original fibre with conc. hydrochloric acid.		
				Colour of fibre yellow to orange.	Fibre becomes reddish-brown.	Fibre unchanged.	Yellow spot.	
1	2	3	4	5	6	7	8	9
Neutral violet, rhoduline violet, rhoduline heliotrope, rosolane, methylene violet, methyl heliotrope, tannin heliotrope, iris violet, etc.	Methyl violet, ethyl violet, crystal violet, benzyl violet, brilliant violet, etc.	Soluble red woods, e.g., Brazil wood, lima wood, sapanwood, peachwood, etc.	Fast blue R, red shade indulines, etc.	Certain red-shade acid violets, e.g., acid violet 4 R S and 5 R S, red violet 4 R S, etc.	Red-shade soluble blues.	Pyrone colours, e.g., fast acid violets, violamines, acid violet 4 R, etc.	Acid violets, alkali violet, Guinea violet, formyl violet, kitone violet, etc.	Lanacyl violet, azo acid violet, indo violet, sulphon violet, Victoria violet, erio fast purple, wool violet.

Div. 1.—Cresyl fast violet 2 B returns in air to a greenish blue instead of to a violet. Its acetic acid extract has a strong group reduce much more slowly than those of the triphenylmethane series. Violamine 3 B falls into Table LVII. *Div.* 8.—Acid in air and usually through green (except ciba heliotrope). *Div.* 14.—Chrome violet (old) gives coloured extracts both with dilute

LVI

Colours on Wool

with 5 per cent. acetic acid.

Dyestuff. Boil twice for one minute with aqueous alcoholic ammonia (1 : 100) and a piece of white cotton.

		Little or no colour is stripped : **Vat, Mordant, or Salt Dyestuff.** Boil with Hydrosulphite A X.						
Colour is changed to orange-yellow, restored by persulphate to a violet-brown : *Anthraquinone Class.*	Colour unaffected : *Pyrone Class.* A chrome mordant is present.	Decolorised. Colour returns on exposure to air. Test for a mordant. — Mordant present : *Azine, Oxazine, or Thiazine Class.*	Mordant absent : *Indigoid Vat Dyestuff.* Confirm by extraction with aniline and sublimation.	Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenyl-methane Class.* A chrome mordant is present.	Decolorised. Colour is not restored either by air or by persulphate : *Azo Class.* Test for a mordant (Cr). — Mordant present : *Acid-mordant Dyestuff.*	Mordant absent : *Salt Dyestuff.* Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton. Stained.	Colour changed to orange-brown or brown : *Alizarine Class.* A mordant is present. Boil original fibre with dilute hydrochloric acid (1 : 10). — Fibre and solution orange.	Fibre and solution red-brown to violet-brown.
10	11	12	13	14	15	16	17	18
Anthraquinone violet, alizarine direct violet, alizarine irisol, alizarine cyanol violet, erweco alizarine acid blue.	Galleine.	Gallocyanine, prune, celestine blue, corceine.	Helindone violet, ciba violet, ciba heliotrope, thioindigo violet, etc.	Chromogene violet, metachrome violet, chrome violet.	Acid alizarine violet, acid chrome violet, eriochrome violet, palatine chrome violet, oxychrome violet.	Diamine, benzo, dianil, Columbia, chlorazol, naphthamine, chlorantine, etc., violets.	Alizarine red S, etc., on Fe.	Alizarine Bordeaux, alizarine claret, alizarine maroon.

red fluorescence. Brilliant rhoduline violet R is a rhodamine and comes into Table IX. *Div. 7.*—The dyestuffs of the pyrone violet 7 B gives a bright green spot with concentrated hydrochloric acid. *Div. 13.*—The indigoid " vat " colours only return slowly acetic acid and with dilute ammonia, but the fibre is not markedly stripped.

Blue Colours

Boil twice for one minute

Much colour is stripped : **Basic Dyestuff** or **Logwood.** Boil with dilute alcohol (1 : 1) twice for one minute.				Little or no colour is stripped : **Acid, Vat, Mordant,** or **Salt Dyestuff.** Boil								
Much colour is stripped : **Basic Dyestuff.** Boil with Hydrosulphite A X.			Un-affected. Al or Cr is present in ash. On spotting with hydro-chloric acid, the blue is changed to brick-red.	Much colour is stripped, but cotton remains white : **Acid Dyestuff.** Boil with Hydrosulphite A X.								
				Decolorised. Colour returns on exposure to air : *Azine, Oxazine, Thiazine,* and *Indigo* Classes. Also *Prussian Blue.*			Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenyl-methane Class.*			Fibre is not decolorised, but colour changes : *Anthraquinone* Class. Colour of reduced fibre is :	
Decolorised. Colour returns on exposure to air : *Azine, Oxazine,* or *Thiazine Class.*	Decolorised. Colour does not return on exposure to air, but is restored by per-sul-phate : *Triphe-nylme-thane Class.*	Decolorised. A violet colour returns on exposure to air : *Safran-ine Azo Dye-stuff.*		The ammoniacal extract is blue. On adding caustic soda		The ammo-niacal extract is colour-less. Fe is present in ash.	Ammoniacal extract is blue. Treat fibre with cold conc. sul-phuric acid.		Ammo-niacal extract is colour-less, but becomes blue on acidify-ing.	De-colorised. Colour is not restored either by air or by persul-phate : *Azo Class.*	red-violet, return-ing with persul-phate.	bright yellow to orange-brown, return-ing with persul-phate.
				at once becomes yellow.	becomes violet on heating.		Fibre and solution red-brown to orange-brown.	Fibre and solution colour-less to pale yellow.				
1	2	3	4	5	6	7	8	6	10	11	12	13
Methylene blue, Nile blue, Capri blue, cresyl blue, Meldola's blue, new methylene blue, diphene blue, etc.	Night blue, Victoria blue, setocyanine, setoglaucine, turquoise blue, etc.	Janus blue, diazine blue, indoine blue, Janus dark blue, naphthindone, etc.	Logwood blue.	Indigo extract, indigo carmine.	Thiocarmine, fast blue, induline, acid cyanine, fluorescent blue, lazuline blue, etc.	Prussian blue.	Wool blue, cyanole F F, intensive blue, etc.	Patent blue, new patent blue, Neptune blue, xylene blue, brilliant acid blue, kitone blue, erioglaucine, eriocyanine, eriochlorine, cyanole, cyanine, fast acid violet 10 B, cyanogene, etc.	Soluble blue, water blue, alkali blue, chlorazol brilliant blue 14 B, isamine blue 8 B, betamine blue 8 B, brilliant dianil blue 6 G, brilliant sky blue 8 G, direct blue 12 B, etc.	Lanacyl blue, azo acid blue, azo merino blue, azo navy blue, chromazone blue, azocyanine, orthocyanine, etc.	Alizarine saphirol, anthracyanine, alizarine direct blue E B and E 3 B, alizarine cyanol E F, brilliant anthrazurol, eriocyanine L M, fast sky blue, etc.	Alizarine astrol, alizarine uranol, cyananthrol, alizarine direct blue B, alizarine cyanol B, alizarine sky blue, anthraquinone blue, etc.

Div. 1.—Certain "basic mordant" dyestuffs belonging to Div. 17 (celestine blue B, correine 2 R, gallocyanine, etc.) tend to 9.—All the dyestuffs of the patent blue class are somewhat difficult to strip with dilute ammon.., some of the new marks being sky blues, are mixtures of the pure dyestuff represented by the bluest marks (triphenylmethane compounds) with a disazo dyestuff blue. These dyestuffs are probably mixtures. *Div.* 18.—Many of the blues and navy blues of the eriochrome series are mix are azo mordant colours, as is also eriochrome dark blue B. *Div.* 19.—Helindone grey and thioindigo grey fall into this group The sulphoncyanines and sulphonazurines only stain cotton in sodium acetate solution upon long boiling. Brilliant sulphonazurin

LVII

on Wool

with 5 per cent. acetic acid.

twice for one minute with dilute ammonia (1 : 100) and a piece of white cotton. Keep the ammoniacal extract.

Little or no colour is stripped : **Vat, Mordant,** or **Salt Dyestuff.** Boil with Hydrosulphite A X.

Colour unaffected, or slightly darker : *Anthraquinone Class*. Test for a mordant (Cr).		Decolorised. Colour returns on exposure to air. Test for a mordant.					Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenylmethane Class*. Test for a mordant.		Decolorised. Colour is not restored either by air or by persulphate : *Azo Class*. Test for a mordant.			Colour changed to brown, becoming blue again on exposure to air : *Alizarine Class*. Mordant present.
		Mordant present : *Azine, Oxazine,* or *Thiazine Class*. Treat fibre with cold conc. sulphuric acid.		Mordant absent. Treat fibre with aniline.					Mordant present. Boil with 5 per cent. sodium acetate and a piece of white cotton for two or three minutes.		Mordant absent : *Salt Dyestuff*. Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton. Cotton stained.	
Mordant present.	Mordant absent.	Fibre and solution green.	Fibre and solution blue or violet.	Fibre and solution red.	Blue solution giving on evaporation a sublimable residue : *Indigoid Vat Dyestuff*.	Colourless solution : *Pyrone Dyestuff*.	Mordant present.	Mordant absent.	Cotton remains white : *Acid-mordant Dyestuff*.	Cotton is stained : *Salt-mordant Dyestuff*.		
14	15	16	17	18	19	20	21	22	23	24	25	26
Alizarine cyanine, brilliant alizarine cyanine, anthracene blue, alizarine indigo blue, acid alizarine blue 2 B and G R, etc.	Indanthrene blue W B.	Brilliant alizarine blue, mercerol brilliant blue, indochromine, etc.	Gallocyanine, celestine blue, correine, prune, gallamine blue, delphine blue, brilliant delphine blue, indalizarine, lanoglaucine, ultra cyanine, ultra violet, etc.	Eriochrome azurol, eriochrome cyanine, chrome worsted blue, chromal blue, chromoxane blue, etc.	Indigo, helindone blue 3 G and 2 B, ciba blue, thioindigo blue, etc.	Fast acid blue R, violamine 3 B.	Chrome blue.	Brilliant milling blue B.	Cyprus blue, chromotrope blue, acid chrome blue, chrome fast blue, anthracene chrome blue, fast mordant blue, salicine chrome blue, monochrome blue, etc.	Autochrome blue.	Diamine, benzo, dianil, Chicago, chlorazol, naphthamine, etc., blues and sky blues, sulphon acid blue, sulphoncyanine, sulphonazurine, erio fast blue S W R, tolyl blue G R extra and 5 R extra, etc.	Alizarine blue (*Anthraquinone Class*).

strip slightly with boiling 5 per cent. acetic acid. *Div. 8.*—Certain brands of wool blue are mixtures containing patent blue. *Div.* barely affected. *Div. 10.*—The redder brands of the chlorazol brilliant blues, isamine blues, brilliant dianil blues, and brilliant of Div. 25. *Div. 13.*—The cyananthrols and alizarine sky blues are restored by persulphate to a slate grey instead of to the original tures, apparently of eriochrome azurol or of eriochrome cyanine with " mordant " azo dyestuffs. Eriochrome blue S, B, and B R *Div. 21.*—Chrome blue A is a mixture of a chromotrope with a little patent blue. Chrome blue B is also a mixture. *Div. 25.*— is reduced by hydrosulphite to a pink, which is only decolorised with great difficulty.

Green Colours

Boil twice for one minute

Much colour is stripped : **Basic Dyestuff.** Boil with Hydrosulphite A X.			Little or no colour is stripped : **Acid, Vat, Mordant,** or **Salt**					
			Much colour is stripped, but cotton remains white : **Acid Dyestuff.** Boil with Hydrosulphite A X.					
Decolorised. A dark violet colour returns on exposure to air : *Safranine Azo Dyestuff.*	Decolorised. Original colour returns on exposure to air : *Azine, Oxazine,* or *Thiazine Class.*	Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenylmethane Class.*	Decolorised. Colour returns on exposure to air : *Azine, Oxazine,* or *Thiazine Class.*	Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenylmethane Class.*	Decolorised. Colour is not restored either by air or persulphate : *Azo Class.*	Fibre is not decolorised, but colour changes : *Anthraquinone Group.* Colour of reduced fibre is : Red-violet returning with persulphate to bluish-green.	Orange returning with persulphate to grey-green.	Decolorised, returns on air. Test for Mordant present : *Oxazine* or *Thiazine Class.*
1	2	3	4	5	6	7	8	9
Janus green, diazine green.	Methylene green, Capri green, azine green, fast green M, etc.	Malachite green, brilliant green, fast green, setoglaucine, solid green, China green, new fast green, etc.	Azine green S.	Acid green, light green, Guinea green, wool green, Neptune green, naphthalene green, alkali fast green, cyanole fast green, agalma green, erioviridine, erio green, brilliant milling green B, night green, etc.	Sulphon acid green, mixtures of an azo blue and yellow.	Alizarine emeraldol, alizarine direct green.	Anthraquinone green, alizarine cyaniné green, alizarine trilliant green, fast acid green R H, anthraquinone blue-green.	Alizarine green B and G.

General.—As green shades are frequently produced with mixtures of blue and yellow dyestuffs, Tables LIV and LVII shoul fall into Table LVII.   *Div. 8.*—Anthracyanine greens 3 G L and B L, though mixtures, fall into this group.   *Div. 13.*—Eriochrom

LVIII

on Wool

with 5 per cent. acetic acid.

Dyestuff. Boil twice for one minute with dilute ammonia (1 : 100) and a piece of white cotton.

Little or no colour is stripped : **Vat, Mordant,** or **Salt Dyestuff.** Boil with Hydrosulphite A X.

Colour exposure to a mordant.	Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenylmethane Class.* A Cr mordant is present.	Decolorised. Colour is not restored either by air or by persulphate : *Azo* or *Nitroso Class.* Test for a mordant.				Colour changed to red-violet. The original colour is restored by persulphate. A chrome mordant is present.	Colour changed to orange or orange-brown : *Alizarine Class.*	
		Mordant present. Boil with 5 per c.nt. sodium acetate and a piece of white cotton.			Mordant absent : *Salt Dyestuff.* Confirm by boiling with 5 per cent. sodium acetate and a piece of white cotton.			
Mordant absent : *Indigoid Vat Dyestuff.* Confirm by extraction with aniline and sublimation test.		Cotton remains white. Boil original fibre with conc. hydrochloric acid.		Cotton is stained : *Salt-mordant Dyestuff.*			Original colour returns on exposure to air. A mordant is present.	Original colour does not return on exposure to air, but is restored by persulphate. A chrome mordant is present.
		Fibre and solution light brown : *Ni'roso Class.*	Colour of fibre unchanged, or bluer : *Azo Class.*					
10	11	12	13	14	15	16	17	18
Ciba green G, helindone green G.	Chromoxane green, chrome green, fast chrome green, etc.	Naphthol green B, gambines, dioxine, chrome green G, etc.	Diamond green B and 3 G, chromoxal green, cyprus green, omega chrome green, eriochrome green H and L, acid chrome green, chrome fast green, etc.	Diamond green 2 S, chrome patent green N, mercerol green, etc.	Diamine, benzo, dianil, Columbia, chlorazol, naphthamine, etc., greens.	Eriochrome verdone, acid alizarine green.	Coeruleine, alizarine green S, alizarine dark green W.	Alizarine cyanine green, alizarine viridine, brilliant alizarine viridine, etc.

also be consulted. *Div.* 5.—Brilliant milling green S is a dyestuff of the patent blue class, and on account of its shade would olive, upon treatment with concentrated HCl, gives a crimson solution and fibre.

TABLE

Brown Colours

			Boil twice for one minute	
Much colour is stripped : **Basic Dyestuff.** Boil with Hydrosulphite A X.		Little or no colour is stripped : **Acid, Vat,**		
		Much colour is stripped : **Acid Dyestuff.** On boiling with Hydrosulphite A X, decolorised. Colour is not restored either by air or by persulphate : *Azo Class.*	Little or no	
Decolorised. A violet colour returns on exposure to air : *Safranine Azo Dyestuff.*	Decolorised. Colour is not restored either by air or by persulphate : *Azo Class.*		Decolorised. Colour returns on exposure to air. Boil with 5 per cent. sodium acetate and a piece of white cotton for two minutes.	
			Cotton remains white : *Indigoid Vat Dyestuff.*	Cotton is stained : *Salt Dyestuff, Stilbene Class.*
1	2	3	4	5
Diazine brown.	Bismarck brown, Janus brown tannin brown.	Acid brown, fast brown, resorcin brown, supramine brown, Guinea brown, solid brown, sulphon acid brown, Neptune brown, wool brown, etc.	Helindone brown, ciba brown, thioindigo brown, etc.	Mikado browns.

General.—Brown shades are very frequently dyed with mixtures of dyestuffs, e.g., with an orange shaded with a blue or viole
1.—Diazine brown might be classed as a violet.   *Div.* 3.—Anthracyanine browns G L and R L, which are mixtures, fall into th
gives a rose-coloured strip with dilute ammonia.   *Div.* 4.—The " vat " colours after reduction return in air much less rapidly tha
brown R, unlike the other vat browns, does not reduce to a pale yellow but to a yellowish brown.   *Div.* 7.—A number
brown G is a mordant azo dyestuff.   *Div.* 10.—Cutch in heavy shades is liable to be slightly stripped by hydrosulphite A

LIX

on Wool

with 5 per cent. acetic acid.

Mordant, or **Salt Dyestuff.** Boil twice for one minute with dilute ammonia (1 : 100).

colour is stripped : **Vat, Mordant,** or **Salt Dyestuff.** Boil with Hydrosulphite A X.

Decolorised. Colour does not return on exposure to air, but is restored by persulphate.	Decolorised. Colour is not restored either by air or by persulphate : *Azo Group*. Boil with 5 per cent. sodium acetate and a piece of white cotton for two minutes.		Colour of fibre unaltered. Boil with dilute hydrochloric acid (1 : 10).	
	Cotton remains white. Cr is present. *Acid-mordant Dyestuff*.	Cotton is stained. Cr may be present. *Salt Dyestuff*.	Colour is stripped. Cr present.	Colour is not stripped. Cr and Cu present.
6	7	8	9	10
Chromogen, oxychromine.	Anthracene acid brown, acid anthracene brown, acid alizarine brown, anthracene chromate brown, diamond brown, acid chrome brown, palatine chrome brown, salicine brown, oxychrome brown, metachrome brown, monochrome brown, mercerol brown, etc. Also Manganese brown (Mn in ash).	Diamine, benzo, dianil, Columbia, Congo, naphthamine, toluylene, hessian, etc., browns.	Anthragallol, anthracene brown, alizarine brown.	Cutch.

for which colours the respective tables must be consulted. The commercial brown dyestuffs are also frequently mixtures. *Div.* group. On reduction with hydrosulphite A X and oxidation with persulphate, a blue or grey-blue is obtained. Fast brown G do the stilbenes. Helindone brown C R in particular returns very slowly, and should be confirmed by solubility in aniline. Ciba " mordant " azo browns appear to stain cotton very slightly on long boiling with sodium acetate solution. *Div. 9.*—Alizarine becoming more orange.

Boil twice for one minu

	Little or no colour is stripped : **Acid, Mordant,** or **Salt Dyestuff.**				B
	The colour is stripped : **Acid** or **Salt Dyestuff.**		Little or no colour		
Much colour is stripped : **Basic Dyestuff.**	The cotton remains white : **Acid Dyestuff.** On boiling with Hydro-sulphite A X, the colour is permanently discharged.	The cotton is stained : **Salt Dyestuff.** On boiling with Hydro-sulphite A X, the colour is permanently discharged.	Fibre and solution crimson.	Fibre and solution orange to pale brown.	Fibre blue or blue-violet, solution crimson. Test for indigo by extraction, evaporation, and sublimation.
1	2	3	4	5	6
Janus black, diazine black, jute black, methylene grey, new fast grey, etc.	Naphthol black, naphthylamine black, nerol, amido black, amine black, azo acid black, azo merino black, palatine black, supramine black, sulphoncyanine black, sulphon black, Biebrich patent black, cresol black, Guinea black, etc.	Union black, Columbia, diamine, dianil, benzo, chlorazol, naphthamine, etc., blacks and fast blacks, carbide black, direct deep black, direct blue black, chromanil black, cotton black, etc.	Logwood on Cr.	Logwood on Fe, Bonsor's black.	A " vatted black " (indigo and logwood).

General.—The reduction of black colours with hydrosulphite seldom gives rise to a pure white, the shade obtained usually having giving blue or violet liquids, but the colour of the fibre is little altered.

LX

Colours on Wool

with 5 per cent. acetic acid.

twice for one minute with aqueous alcoholic ammonia (1 : 100) and a piece of white cotton.

stripped : **Mordant Dyestuff.** Boil for half a minute with dilute hydrochloric acid (1 : 10).

		Fibre unaffected. Boil with Hydrosulphite A X.		
Unaffected. Treat original fibre with cold conc. sulphuric acid.		The colour is discharged. Boil for one minute with 5 per cent. sodium acetate and a piece of white cotton.		Colour changed to brown. Original colour returns slowly on exposure to air.
Blue solution.	Colourless solution.	Cotton remains white.	Cotton is stained.	
7	8	9	10	11
Alizarine cyanine black.	Aniline black.	Diamond black P V, P V B, P 2 B, F, diamond blue black E B, eriochrome black, eriochrome grey, chrome fast black, anthracene chrome black, acid alizarine black, fast chrome black, acid chrome black, acid alizarine grey, autochrome grey, etc.	Diamond black F B, F R, N G, G A, 2 B, palatine chrome black, anthracene acid black, alizadine black, monochrome grey, anthracene chromate grey, etc.	Naphthazarine, alizarine blue black S W, W, brilliant alizarine black, alizarine black S, W R, W X, etc.

a brownish or greyish tint. *Divs.* 9 *and* 10.—Many salt and mordant blacks bleed when boiled with dilute hydrochloric acid,

(b) Investigation of Colouring Matters fixed on Cotton. Investigation of the nature of the dye or printing on cotton usually presents greater difficulties than are encountered with dyed woollen goods.

The following points call for notice :

1. The presence of tannin—used in dyeing with certain basic colouring matters—hinders the removal of the latter by dilute acetic or formic acid. The tannin is consequently expelled by treatment with boiling caustic soda solution. Since, however, this alkali solution might loosen also the colouring matter, it is saturated with sodium chloride. Under these conditions basic colouring matters remain on the fibre as free bases and may be removed easily by boiling, dilute acetic acid or, better, formic acid.

Most other colouring matters withstand the action of the salted caustic soda, but some mordant colours, such as Turkey red, are partly decomposed by it. In these last cases, therefore, the extract obtained with acetic or formic acid does not usually exhibit the colour of the sample under investigation. In order to avoid any possibility of error, when the colouring matter has been removed in appreciable quantity, it is advisable to add a solution of tannin to the acid extract : in presence of a basic colouring matter, a precipitate will be formed.

Basic mordant colouring matters (gallocyanin, etc.), if treated with salted caustic soda and then with formic acid, behave like basic colouring matters, except that they are extracted less completely. The acid extracts give with tannin a finer and less distinct precipitate. To distinguish them from ordinary basic colouring matters use is made of the fact that they are precipitated by chromium fluoride.

2. Certain basic colouring matters fixed on tannin are not reduced by hydrosulphite, or if the leuco-derivative is formed, this passes into solution, so that reoxidation on the fibre is impossible. This inconvenience is avoided by transferring the colouring matter to wool and then testing this with hydrosulphite and persulphate. Such transference from cotton to wool is easy after the elimination of the tannin as above and is of advantage with lightly dyed cotton goods, since the colour from a large amount of the sample may be collected on a small piece of wool, the tests being thus rendered sharper. Further, with a mixture of colouring matters, such transference often renders possible a separation of the various colouring bodies, since these usually possess different affinities for wool.

3. With acid colouring matters, transference to wool is also carried out before the reduction and oxidation tests.

4. Colouring matters which are neither acid nor basic are reduced and oxidised on the cotton itself. The resistance to reduction exhibited by certain azo-colouring matters, especially those formed directly on the fibre, is overcome by addition of very small quantities of suitable colouring matters or other reducing bodies, such as indulin scarlet, alizarin or anthraquinone, which increase the activity of the hydrosulphite. The use of anthraquinone is preferred because it does not dye cotton, while addition of it in minimal quantity to the hydrosulphite solution and slight acidification with acetic acid yields a reagent (hydrosulphite B X) which causes reduction in every case.

5. For the identification of the sulphide colouring matters, use is made of the reaction with stannous chloride, which may however in certain cases lead to error in consequence of the presence of other sulphur compounds, such as bisulphite compounds, ultramarine, etc., capable of yielding hydrogen sulphide under the experimental conditions used. Further, many direct dyestuffs, although not sulphur colouring matters, evolve hydrogen sulphide when heated with stannous chloride, possibly owing to reduction of the sulphonic groups. It is necessary, therefore, to exclude the presence of direct dyestuffs before testing for sulphur colouring matters.

Reagents. The reagents necessary for investigating the nature of dyes on cotton are :

1. 1% ammonia solution (1 c.c. of ammonia of D = 0·884 to 100 c.c. of water).

2. 10% aqueous sodium hydroxide.

3. Saline caustic soda (10 c.c. of 35–40% NaOH solution in 100 c.c. of saturated NaCl solution).

4. 90% formic acid solution.

5. 1% formic acid solution (1 c.c. of 90% formic acid solution in 100 c.c. of water).

6. Dilute hydrochloric acid (5 c.c. of hydrochloric acid of D = 1·52—i.e., about 30%—in 100 c.c. of water).

7. 5% sodium carbonate solution or 10 grams of Marseilles soap dissolved in 300 c.c. of water.

8. Tannin solution (10 grams of tannin and 10 grams of sodium acetate in 100 c.c. of water).

9. Calcium hypochlorite solution (3·4° Baumé = sp. gr. 1·025).

10. Hydrosulphite B and A X (*see* p. 472).

11. Hydrosulphite B X : 50 grams of hydrosulphite N F conc. or of rongalite are dissolved in 125 c.c. of hot water. 1 gram of precipitated (not sublimed) anthraquinone is ground to a fine powder and made into a paste with a little of the above solution. This paste is added to the hot solution of hydrosulphite and heated to 90° C. for 1–2 minutes, being then made up with cold water to 500 c.c. and, when cold, mixed with 1·5 c.c. of glacial acetic acid. This reagent is stored in a tightly closed bottle with a greased ground stopper, and it should be tested from time to time, before use, with cotton dyed by a-naphthylamine bordeaux, which should be fully discharged after 1–2 minutes' boiling.

12. Stannous chloride : 100 grams of stannous chloride are dissolved in 100 c.c. of about 30% pure hydrochloric acid diluted with 50 c.c. of water. It may be replaced, in investigating sulphur dyes, by concentrated titanium chloride solution.

13. Chromium fluoride (10 grams of chromium fluoride and 5 grams of sodium acetate in 100 c.c. of water).

14. Saturated, cold aqueous solution of potassium persulphate or 1% aqueous ammonium persulphate (*see* note on p. 472).

Procedure. In general this is as indicated for the investigation of dyestuffs fixed on wool (*see* p. 471). With goods printed in various colours the differently coloured parts should be separated and examined apart.

As regards the different cases which may present themselves, the following points should be borne in mind :

1. Stripping test for acid colours. Some direct or " salt " dyestuffs are partly decolorised by dilute ammonia and hence might be regarded as acid colouring matters. To avoid this error it is useful to add, when this test is made, a piece of mercerised white cotton. With an acid dye, the cotton remains white, or is scarcely coloured, and then becomes white again when boiled a second time with dilute ammonia.

2. Transference of basic colouring matters to wool. The tannin is first eliminated by boiling the sample for half a minute with the saline caustic soda. It is then well washed with cold water (or, if the base is soluble, with salt water) to remove all the alkali and is afterwards boiled with a piece of white wool—usually about one-half, or less than one-half, as much as the cotton—in a little water for 1-2 minutes. As a rule the base of the colouring matter is removed almost completely from the cotton and gives a full colour to the wool. If the colour does not develop well on the wool, 1–2 drops of dilute formic acid (1%) are added. In certain exceptional cases, after the treatment with the saline caustic soda, it may be necessary to extract the colouring matter with hydrochloric acid (1 : 20), the liquid being carefully neutralised with ammonia before adding the wool.

3. Transference of acid dyes to wool. The fabric is boiled in presence of a small quantity of wool with 1% formic acid.

4. Tannin test for basic dyestuffs. The extract obtained with formic acid is shaken with a few drops of tannin solution, and if no precipitate forms immediately, the liquid is left at rest for a few minutes. Certain colouring matters, such as the rhodamines, the gallocyanins and the chrome colours of the rosaniline series (containing carboxyls or hydroxyls besides the basic groups) precipitate slowly and the precipitate, being highly subdivided, is sometimes difficult to see.

5. Test for salt colouring matters. A piece of the fabric is boiled in the soap or sodium carbonate solution in presence of white mercerised cotton to see if the cotton remains coloured.

6. Test for sulphide dyestuffs. The sample is covered in a test-tube or conical flask with the acid stannous chloride solution, the mouth of the vessel being closed with a piece of filter-paper steeped in lead acetate solution and the liquid heated slowly to boiling. The appearance of a blackish-brown stain on the filter-paper indicates a sulphur dyestuff. The boiling should not be too protracted, since otherwise the hydrochloric acid vapours may cause the brown lead sulphide to disappear.

To avoid errors due to the presence of extraneous sulphur compounds in the cotton, the latter may be boiled for half a minute—before testing—with 10% caustic soda solution and then boiled well with water. It must, however, be borne in mind that the reaction of the sulphide dyestuffs is thus rendered less distinct. Use should not be made in this test—unless after thorough washing—of test-tubes or flasks previously used for the hydrosulphite reduction, since the latter results in the deposition on the glass of an imperceptible layer of sulphur, which may lead to evolution of hydrogen sulphide in presence of the boiling solution of the tin salt.

7. Reduction and reoxidation tests. Reduction with hydrosulphite B X is effected by boiling the fabric in this reagent for about two minutes. Azines, thiazines, oxazines, etc., and most of the azo-dyestuffs are completely reduced in about half a minute, but insoluble azo-dyestuffs require more prolonged boiling for their complete reduction.

In reoxidation by means of the air, the reduced sample may be exposed to ammonia vapour, which in many cases accelerates the reoxidation. If the colour does not reappear under these conditions, treatment with a cold, saturated potassium persulphate solution or with 1% ammonium persulphate solution is tried in accordance with the indications given for woollen fabrics (see p. 473).

8. Test for vat dyestuffs. By means of the tables given below vat dyestuffs may be distinguished from those of other groups, and in most cases indigoid vat dyestuffs from those derived from anthracene. The exact identification of the vat dyestuff used in dyeing a given product is not always easy. For this purpose use may be made of the reactions and tests given in special memoirs.[1]

9. Tests for mordants. The principal mordants may be detected by the method indicated on p. 473 for their detection in dyed woollen goods. As mordants for cotton goods use is made also of antimony salts and sometimes of nickel salts. If the method referred to is followed, antimony will be identified as sulphide when the hydrochloric acid solution of the disaggregated mass is treated with hydrogen sulphide ; nickel will be identified as sulphide, separated by the action of ammonium sulphide on the filtrate obtained after the treatment with ammonium chloride and ammonia.

With goods mordanted with antimony salts, the platinum dish may be slightly attacked during the disaggregation of the ash. This inconvenience may be avoided by using the method given in the note on p. 474, when the presence of antimony is suspected. In this case, however, the undissolved part left after treatment with zinc and sulphuric acid should be acted on with aqua regia.

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[1] A. G. Green and G. H. Frank : The reactions of the Vat Dyestuffs upon Cotton Fibre, *Journ. Soc. Dyers and Colourists*, 1910, XXVI, p. 83.

TABLES

For the Identification of Artificial Organic Colouring Matters on Cotton

TABL

Yellow and Orang

Boil with we

The colour is stripped. Boil with acidified water and small piece of white wool.			The colour is not stripped. Boil for a quarter of a minute with sali						
	Colour is transferred to the wool: **Acid Dyestuff.** Boil wool with Hydrosulphite B.		The colour is completely destroyed, both solutions and fibre being colourless. Treat original fibre with cold ammonium sulphide.				The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution: **Basic Dyestuff.** Transfer to wool and boil with Hydrosulphite B.		
				Fibre is not blackened. Boil with Hydrosulphite B X.			Wool is not decolorised. Boil cotton with hydrochloric acid (1 : 20).		
Colour not transferred to the wool. Sn is present in ash.	Not decolorised: *Pyrone* or *Quinoline Class.*	Permanently decolorised: *Azo Class.*	Fibre blackened. Cr present in ash.	Not decolorised. Test for Al in ash.		De-colorised.	De-colorised.	Not decolorised. The conc. H_2SO_4 and alcoholic solutions are fluorescent: *Acridine Class.*	Wool is permanently decolorised: *Azo Class.*
				Al present.	Al absent.				
1	2	3	4	5	6	7	8	9	10
Persian Berries on tin mordant.	Quinoline yellow, eosine orange.	Indian yellow, orange IV, G, etc.	Chrome yellow or chrome orange (lead chromate).	Alizarine yellow A.	Thioflavine T, methylene yellow, rhoduline yellow.	Flavinduline.	Auramine.	Phosphine, benzoflavine, acridine yellow, corisphosphine, rheonine, patent phosphine, flavophosphine, aurophosphine, acridine orange, etc.	Chrysoidine, tannin orange, Janus yellow, azo phosphine, new phosphine, etc.

Div. 1.—Brilliant yellow is largely stripped by weak ammonia, but if white cotton is present it will be stained.   *Div. 2.*
in soap.   *Div.* 3.—Auramine G is almost completely stripped by saline caustic soda, and the formic extract therefore gives
Helindone yellow and helindone orange give yellow vapours on heating the fibre in a dry tube.   Upon reduction with hydrosulphi
hydrosulphite B X to a blue, indanthrene golden orange remains unchanged.
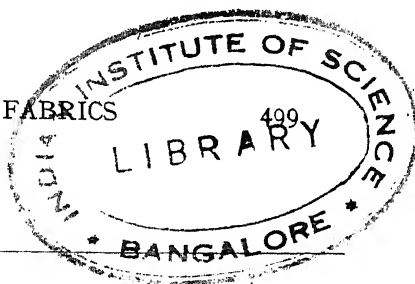
LXI

Colours on Cotton

mmonia (1 : 100).

austic soda, rinse with cold water, and boil with water, and one or two drops of weak formic acid (1 : 100).

A coloured acid extract precipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite B X.							
Decolorised or becomes light yellow. Original colour is not restored by air oxidation : *Azo Dyestuff* (including the *Stilbene Class*). Boil with soap solution and white mercerised cotton.				The colour is unaffected or changed in shade, becoming lighter, browner, or bluer. If altered in shade, exposure to air restores the original colour. Apply the lead acetate test.			
White cotton is stained : **Salt Dyestuff.**		White cotton is not stained. Boil with pyridine.			No H₂S is evolved. Boil with soap solution and white mercerised cotton.		
						The white cotton is not stained : **Mordant or Vat Dyestuff.** Boil with 90 per cent. formic acid. Also test ash for metallic mordant.	
Fibre after reduction is light yellow and can be diazotised and developed red with betanaphthol : *Primuline Azo Colour.*	Fibre after reduction is colourless : *Salt Azo Dyestuff.*	Colour is stripped : *Insoluble Azo Colour.*	Colour is not stripped. Cr present in the ash : *Azo Mordant Dyestuff.*	H₂S is evolved : *Sulphide Dyestuff.*	The white cotton is stained : *Thiazol Salt Dyestuff.*	Colour stripped by formic acid. Al or Cr in ash : *Mordant Dyestuff.*	Colour not stripped by formic acid. No mordant in ash : *Vat Dyestuff.*
11	12	13	14	15	16	17	18
Primuline developed with phenol or with resorcinol, cotton yellow G and R, oriol yellow, dianil yellow, etc.	Chrysophenine, chrysamine, carbazol yellow, toluylene yellow and orange, stilbene yellows and oranges, benzo, Congo, diamine, and dianil yellows and oranges, pyramine orange, Pluto orange, etc.	Metanitraniline orange, nitrotoluidine orange, orange from naphthol A C.	Chrome orange, alizarine yellow R, G G, etc., diamond flavine, flavazol, etc.	Yellows and oranges of the immedial, katigene, cross-dye, pyrogene, thiogene, sulphur, thional, etc., series.	Chlorophenine, chloramine yellow, diamine fast yellow B, F F, and C, Clayton yellow, thiazol yellow, thioflavine S, etc. Primuline developed with hypochlorite.	Persian berries on Al or Cr mordants, alizarine orange on Al mordant.	Helindone orange R, helindone yellow 3 G, anthraflavone G, algole yellow 3 G and R, indanthrene yellow, indanthrene orange R T and golden orange, algole orange R, indanthrene copper, cibanone yellow R and orange R.

Sulphide yellows of the thiazol class, such as katigene yellow 2 G, pyrogene yellow, etc., stain white cotton slightly when boiled precipitate with tannin solution. *Div. 4.*—Diamond flavine, if not fully fixed, may stain cotton from a soap solution. *Div. 5.*— B X, helindone yellow becomes olive, helindone orange colourless. *Div. 6.*—Indanthrene yellow (flavanthrene) is reduced by

TABL...

Red Colour...

Boil with wea...

The colour is not stripped. Boil for a quarter of a minute with saline caustic sod...

The colour is stripped: **Acid Dyestuff.** Transfer to wool and boil with Hydrosulphite A X.		The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution: **Basic Dyestuff** (on tannin or other mordant). Transfer to wool and boil with Hydrosulphite A X.				A colour... Decolorised and colo... persulphate: *Azo Clas...* white mercer...	
						The white cotton is stained: **Salt Dyestuff.** Test ash for Cr and Cu.	
Not decolorised: *Pyrone Class.*	Decolorised. Colour not restored by air or persulphate: *Azo Class.*	Wool not decolorised: *Pyrone Class.*	Wool decolorised. Colour returns on exposure to air: *Azine Class.*	Wool decolorised. Colour does not return on exposure to air, but is restored by persulphate: *Triphenyl-methane Class.*	Wool decolorised. Colour not restored by air or by persulphate: *Azo Class.*	No Cr or Cu present: *Azo Salt Dyestuff.*	Cr or Cu present: *Azo Salt Dyestuff after-treated.*
1	2	3	4	5	6	7	8
Eosines, phloxine, erythrosine, rose Bengal, etc.	Crocein scarlets, brilliant croceines, palatine scarlet, fast reds, etc.	Rhodamines, rhodines, irisamine, anisoline, rosazein, rhoduline pink, acridine reds, etc.	Safranines, rhoduline reds and pink, azine scarlet, induline scarlet, neutral red, etc.	Magenta, fuchsine, new fuchsine, isorubine, cerise, grenadine, etc.	Janus red.	Benzopurpurine, diamine scarlets, diamine reds, benzo fast scarlets, diazo brilliant scarlet, rosanthrenes, Zambesi red, erica, diamine rose, geranine, rosophenine, etc.	Diamine fast red F, etc.

Div. 6.—Janus claret red does no...

LXII

on Cotton

ammonia (1 : 100).

rinse with cold water, and boil for one minute with water and one or two drops of weak formic acid (1 : 100).

acid extract precipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite B X.

not restored by air or by Boil with soap solution and cotton.		Becomes yellow or colourless. Colour returns on exposure to air: *Azine* or *Indigo Class.* Apply lead acetate test. Also heat fibre in dry tube.		Colour changed to greenish yellow (not restored to original colour by air), which can be diazotised and developed red with betanaphthol: *Primuline Azo Colour.*	Colour unaffected or changed to maroon or brown. Original colour restored on exposure to air: *Anthracene Class.* Boil with 90 per cent. formic acid. Also test ash for mordant.		
	The white cotton is not stained. Boil with pyridine.					Colour but little affected by formic acid.	
The colour is stripped: *Insoluble Azo Colour.*	The colour is not stripped. Cr in ash: *Mordant Azo Dyestuff.*	H_2S is evolved: *Sulphide Dyestuff.*	No H_2S is evolved. Red vapours on heating: *Indigoid Vat Dyestuff.*		Colour stripped by formic acid. Al in ash: *Anthracene Mordant Dyestuff.*	Cr in ash: *Anthracene Mordant Dyestuff.*	Cr absent: *Anthracene Vat Dyestuff.*
9	10	11	12	13	14	15	16
Paranitraniline red, alphanaphthylamine Bordeaux, chloranisidine pink, nitroanisidine pink, scarlet and reds from naphthol A C.	Chrome red, brilliant chrome red, chrome Bordeaux, etc.	Thiogene rubine, etc.	Algole red 5 G and scarlet G, algole pink R, ciba red G and scarlet G, ciba Bordeaux B, helindone red B and 3 B, helindone scarlet S, helindone fast scarlet R, thioindigo red B, thioindigo scarlet, vat red.	Primuline developed with betanaphthol or with R-salt.	Turkey red, alizarine red, alizarine pink, alizarine maroon.	Alizarine, purpurines or alizarine maroon on Cr mordant.	Algole red B, indanthrene red, indanthrene claret, ciba scarlet G.

transfer to wool very easily.

TABLE

Purple and Violet

Boil with weal

The colour is stripped: **Acid Dyestuff.** The colour transferred to wool is decolorised by Hydrosulphite A and restored by persulphate: *Triphenylmethane Class.*	The colour is not stripped. Boil for a quarter of a minute with saline caustic soda, rins						
	The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution: **Basic Dyestuff** (on tannin or other mordant) or **Basic Mordant Dyestuff.** Add chromium fluoride reagent to the extract.						
	Not precipitated: **Basic Dyestuff.** Transfer to wool and boil with Hydrosulphite A X.					Precipitated. Cr is present in ash: **Basic Mordant Dyestuff.** Boil cotton with Hydrosulphite B X	
The ammoniacal solution is colourless, but becomes blue on acidifying.	The ammoniacal solution is violet.	Not decolorised: *Pyrone Class.*	Decolorised. Colour returns on exposure to air: *Azine (Oxazine or Thiazine) Class.*	Decolorised. Colour does not return in air, but is restored by persulphate: *Triphenylmethane Class.*	Decolorised. Colour is not restored by air or persulphate: *Azo Class.*	Decolorised. Colour returns on exposure to air: *Oxazine Class.*	Decolorised only slowly. Colour does not return in air, but is restored by persulphate: *Triphenylmethane Class.*
I	2	3	4	5	6	7	8
Red shades of soluble and alkali blues.	Acid violets, formyl violets, alkali violet, Guinea violet, etc.	Anisoline.	Methylene violet, rhoduline violet, iris violet, neutral violet, tannin heliotrope, etc.	Methyl violets, ethyl violet, benzyl violet, crystal violet, etc.	Janus claret red, etc.	Gallocyanine, modern violet, ultra violet, coreine, prune, etc.	Chrome violet.

Div. 17.—Alizarine on chromium becomes rather

XIII

olours on Cotton

monia (1 : 100).

th cold water (or salt solution), and boil for one minute with water and one or two drops of weak formic acid (1 : 100).

A coloured acid extract precipitated by tannin is not obtained.   Reduce original fibre with Hydrosulphite B X.

Decolorised and colour not restored by air or persulphate: *Azo Class* or *Alizarine on Iron* (decolorised slowly). Boil with soap solution and white mercerised cotton.					Decolorised or yellowish. Colour restored on exposure to air: *Azine, Oxazine, Thiazine,* or *Indigoid Classes.* Apply lead acetate test. Also heat fibre in dry test-tube.			The colour is unaffected or only changed in shade, being restored to original on exposure to air: *Pyrone* or *Anthracene Class.* Test ash for mordant.			
The white cotton is stained: **Salt Dyestuff.** Test ash for Cr and Cu.		The white cotton is not stained. Boil with hydrochloric acid (1 : 20).				No H₂S is evolved. Test ash for mordant.		Al or Cr is present: **Mordant Dyestuff.**		Mordants are absent. Apply lead acetate test.	
No Cr or Cu present: *Azo Salt Dyestuff.*	Cr or Cu present: *Azo Salt Dyestuff after-treated.*	Colour destroyed giving yellow solution. Fe present in ash: *Alizarine Red on Fe Mordant.*	The colour is not stripped. Boil with pyridine.		H₂S is evolved: *Sulphide Dyestuff.*	Cr is present. No coloured vapours on heating: *Mordant Oxazine Dyestuff* (not falling in group 7).	Cr is absent. Coloured vapours on heating: *Indigoid Dyestuff.*	The colour on reduction is unchanged.	The colour on reduction is browner or darker.	H₂S is evolved: *Sulphide Dyestuff.*	No H₂S is evolved: *Anthracene Vat Dyestuff.*
			The colour is stripped: *Insoluble Azo Colour.*	The colour is not stripped. Cr present in ash: *Mordant Azo Dyestuff.*							
9	10	11	12	13	14	15	16	17	18	19	20
Violets of the diamine, benzo, Congo, Hessian, Columbia, chlorazol, chloran-tine, dianil, oxamine, and rosanthrene series.	The preceding coppered or chromed.	Alizarine purple.	Benzidine puce.	Chrome Bordeaux, chrome prune, etc.	Thiogene violet, katigene violet, hydrone violet, etc.	Gallocyanine, modern violet, ultra violet, coreine, etc.	Ciba violet, ciba heliotrope, thioindigo violet, helindone violet.	Gallein, alizarine violet, alizarine claret, alizarine cyclamine, alizarine red on Cr mordant.	Alizarine cyanine 3 B, alizarine Bordeaux.	Thiogene dark red, etc.	Indanthrene violet or violanthrene.

browner on reduction with hydrosulphite B X.

TABLE LXI

Blue Colours on C...

The colour is stripped : **Acid Dyestuff** (or Prussian Blue).		The colour is not stripped. Boil for a quarter of a minute with saline caustic soda, rinse with cold w...								Boil with weak ammon... A coloured acid e...
		The colour is completely or largely stripped, giving a coloured acid extract, which is precitated by tannin solution : **Basic Dyestuff** (on tannin or other mordant) or **Basic Mordant Dyestuff.** Add chromium fluoride reagent to the extract.					Decolorised and colour not restored by air or persulphate : *Azo Class.* Boil with soap solution and white mercerised cotton.			
The extract is colourless, but becomes blue on acidification. Transferred to wool, the blue is decolorised by Hydrosulphite A, and restored by persulphate : *Triphenylmethane Class.*	The extract is colourless and remains so on acidification. FeCl$_3$ gives a blue precipitate.	Not precipitated : **Basic Dyestuff.** Transfer to wool and boil with Hydrosulphite A X.			Precipitated. Cr present in ash : **Basic Mordant Dyestuff.** Boil cotton with Hydrosulphite B X.		The white cotton is stained : **Salt Dyestuff.** Test ash for Cr and Cu		The white cotton is not stained. Colour is stripped by boiling pyridine : *Insoluble Azo Colour.*
		Decolorised. Colour returns on exposure to air : *Azine, Oxazine, or Thiazine Class.*	Colour changes to red just before being decolorised. Colour returns violet or blue : *Safranine Azo Dyestuff.*	Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenylmethane Class.*	Decolorised. Colour returns on exposure to air : *Oxazine Class.*	Decolorised slowly. Colour restored only by persulphate : *Triphenylmethane Class.*	No Cr or Cu present : *Azo Salt Dyestuff.*	Cr or Cu present : *Azo Salt Dyestuff after-treated.*	
1	2	3	4	5	6	7	8	9	10
Alkali blues, soluble blues, chlorazol brilliant blue, isamine blue, betamine blue, brilliant dianil blue, brilliant sky blue.	Prussian blue.	Methylene blue, new methylene blue, Nile blue, Capri blue, indazine, Basle blue, metaphenylene blue, Meldola's blue, fast blue, cresyl blue, rhoduline blue, nitroso blue, etc.	Indoine blue, Janus blue, naphthindone blue, diazine blue, etc.	Victoria blue, night blue, turquoise blue, setocyanine, etc.	Gallocyanine, gallamine blue, celestine blue, prune, coreine, ultracyanine, modern cyanine, etc.	Chrome blue.	Blues of the diamine, benzo, Congo, Columbia, chlorazol, dianzil, oxamine, Chicago, etc., series.	The preceding coppered or chromed.	Dianisidine blue, blue from naphthol A C.

Div. 1.—Alkali blue dyed on a tannin and tin mordant is only

LXIV

on Cotton

mmonia (1 : 100).

cold water (or salt solution), and boil for one minute with water and one or two drops of weak formic acid (1 : 100).

acid extract precipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite B X.

Decolorised or yellowish. Colour is restored on exposure to air: *Azine, Oxazine, Thiazine,* or *Indigo Class.* Apply lead acetate test.				Colour unaffected or becomes darker, browner, etc., the original colour being restored on exposure to air: *Anthracene Mordant* or *Anthracene Vat Dyestuff* (also *Ultramarine*). Boil with 90 per cent. formic acid.			
	No H_2S is evolved. Heat fibre carefully in dry test-tube.		Colour changed to greenish yellow, which can be diazotised and developed red with betanaphthol: *Primuline Azo Colour.*	The colour is stripped. Al in ash. Apply lead acetate test.		The colour is not much affected. Test ash for Cr.	
H_2S is evolved: *Sulphide Dyestuff.*	Violet vapours evolved: *Indigoid Dyestuff.*	No coloured vapour. Cr in ash: *Mordant Thiazine* or *Oxazine* (not falling in group 6).		H_2S is evolved.	No H_2S evolved: *Alizarine Dyestuff.* on Al.	Cr present in ash: *Alizarine Dyestuff.* on Cr.	Cr absent: *Anthracene Vat Dyestuff.*
11	12	13	14	15	16	17	18
Blues of the immedial, katigene, thiogene, pyrogene, sulphur, etc., series, hydrone blues.	Indigo (natural and synthetic), indigo MLB 2 B, 4 B, 5 'B, 6 B, and T, ciba blue, bromindigo F B.	Brilliant alizarine blue, gallocyanine, gallamine blue, prune, ultracyanine, modern cyanine, celestine blue, delphine blue, gallophenine, etc.	Primuline developed with naphthylamine ether.	Ultramarine.	Alizarine cyanines or anthracene blues on Al mordant, erganone blues.	Alizarine blue, alizarine cyanines or anthracene blues or Cr mordant.	Indanthrene blues, algole blues.

partly stripped by weak ammonia, the solution being colourless.

TABLE X

Green Colours

Boil with weak

The colour is not stripped. Boil for half a minute

A coloured acid extract

The colour is stripped: **Acid Dyestuff.** The colour transferred to wool is decolorised by Hydrosulphite A and restored by persulphate : *Triphenylmethane Class.*	The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution : **Basic Dyestuff** (on tannin or other mordant) or **Basic Mordant Dyestuff.** Add chromium fluoride to the extract.				Decolorised and colour not restored by air or persulphate : *Azo* or *Nitroso Class.* Boil with soap solution and white mercerised cotton.			
	Not precipitated : **Basic Dyestuff.** Transfer to wool and boil with Hydrosulphite A X.			Precipitated Cr in ash. Fibre decolorised by Hydrosulphite B X, the colour not returning in air, but restored by persulphate : *Triphenylmethane Class.*	The white cotton is stained **Salt Dyestuff.** Test ash for Cr and Cu.		The white cotton is not stained. Boil with hydrochloric acid (1 : 20).	
	Decolorised. Colour returns on exposure to air : *Azine, Oxazine,* or *Thiazine Class.*	Colour becomes red just before being decolorised. Colour returns violet or green on exposure to air : *Safranine Azo Class.*	Decolorised. Colour does not return on exposure to air, but is restored by persulphate : *Triphenylmethane Class.*		Cr and Cu absent : *Azo Salt Dyestuff.*	Cr or Cu present : *Azo Salt Dyestuff aftertreated.*	Colour destroyed. Fe is present in the ash : *Nitroso Class.*	Not decolorised. Cr is present in the ash : *Mordant Azo Dyestuff.*
1	2	3	4	5	6	7	8	9
Acid greens, Guinea green, Neptune green, naphthalene green, agalma green.	Fast green M, methylene green, azine green, Capri green, etc.	Janus green, diazine green, etc.	Brilliant green, malachite green, methyl green, Victoria green, setoglaucine, new fast green, etc.	Chrome green.	Diamine green, benzo green, Columbia green, chloramine green, etc.	The preceding coppered or chromed.	Russian green, fast green O, steam green, Alsace green, gambines, dioxine, etc.	Diamond green, etc.

Div. 8.—Greens of the nitroso group (Gambines, etc.) may become black on

‹V

. Cotton

ionia (1 : 100).

saline caustic soda, rinse, and boil twice with weak formic acid.

ipitable by tannin is not obtained. Reduce original fibre with Hydrosulphite B X.

The colour is changed to greenish yellow, not restored to green by air, which can be diazotised and developed red with beta-naphthol : *Primuline Azo Class.*	Decolorised. Colour returns on exposure to air : *Azine, Oxazine, or Thiazine Class.* Apply lead acetate test.		The colour is unaffected or changed to red, brown, blue, etc. Test ash for Cr and Ni.							Reduced to yellow. Restored by air oxidation : *Indigoid Dyestuff.*
			The ash contains Cr or Ni : *Anthracene Mordant Dyestuff.*				No Cr or Ni present in ash : *Anthracene Vat Dyestuff.*			
	H₂S is evolved : *Sulphide Dyestuff.*	No H₂S evolved : *Mordant Oxazine (or Thiazine).*	Reduced colour is brownish red. Green restored by persulphate, but not by air. Boiling HCl (1 : 20) gives bright green solution.	Reduced colour is brown. Green shade returns on exposure to air. Boil with hydrochloric acid (1 : 20).			Reduced colour is brownish olive. H₂S evolved on applying lead acetate test.	Reduced colour is dark maroon. Green shade restored by air.	Reduced colour is blue. Green shade restored by air.	
				Colour unaffected. Solution colourless. Cr in ash.	Colour of fibre becomes grey, solution red. Ni in ash.	Colour of fibre rather paler, solution brownish yellow.				
10	11	12	13	14	15	16	17	18	19	20
Primuline developed with amidodiphenylamine,	Greens of the immedial, katigene, thiogene, pyrogene, cross-dye, sulphur, and thionol series.	Gallanilic green, indalizarine, etc.	Alizarine viridine, brilliant alizarine viridine, alizarine cyanine green.	Alizarine green S on Cr mordant.	Alizarine green S on Ni Mg mordant.	Coeruleine, anthracene green.	Indanthrene olive or olivanthrene.	Indanthrene green or viridanthrene leucole dark green B.	Algole green.	Ciba green, helindone green.

duction if the Hydrosulphite B X is insufficiently used (formation of ferrous sulphide).

TABLE LXV

Brown Colours on

Boil with weak ammonia

		The colour is not stripped. Boil for half a minute with ...aline					
		A coloured acid extract precipitab... by tan...					
The colour is stripped : **Acid Dyestuff.** Transferred to wool it is permanently ecolorised by ydrosulphite A X : Azo Class.	The colour is stripped, giving acid extract which is precipitated by tannin solution : **Basic Dyestuff.** The dyestuff transferred to wool is permanently decolorised by Hydrosulphite A X : Azo Class.	Decolorised and colour not restored on exposure to air or by persulphate : Azo Class and Mineral Colours. Boil with soap solution and white mercerised cotton.					
		The white cotton is stained : **Salt Dyestuff.** Test ash for Cr and Cu.		The white cotton is not stained. Boil with pyridine.			
				The colour is stripped : Insoluble Azo Colour. Test ash for Cu.		The colour is not stripped : Mineral Colour. Treat with sodium bisulphite in the cold.	
		Cr and Cu absent : Azo Salt Dyestuff.	Cr or Cu present : Azo Salt Dyestuff after-treated.	Cu absent.	Cu present.	Decolorised.	Not decolorised.
1	2	3	4	5	6	7	8
Fast brown, naphthylamine brown, acid brown, etc.	Bismarck brown, Janus brown, tannin brown, etc.	Browns of the diamine, benzo, Congo, dianil, chlorazol, Columbia, Hessian, oxamine, and toluylene series.	The preceding coppered or chromed.	Para brown (chrysoidine and paranitraniline), benzidine or toludine brown.	Paranitraniline cutch (para red coppered).	Manganese bronze.	Iron buff, khaki (oxides of Cr and Fe).

Div. 8.—Iron buff and khaki may become black on reduction if the

LXVI

on Cotton

mmonia (1 : 100).

aline caustic soda, rinse, and boil twice with weak formic acid (1 : 100).

y tannin is not obtained. Reduce original fibre with Hydrosulphite B X.

			Unaltered or changed in shade, becoming darker, paler, yellower, etc. Apply lead acetate test.			
The shade is changed to greenish yellow, which can be diazotised and developed red with betanaphthol : *Primuline Azo Colour.*	Decolorised and original colour restored by air : *Indigoid Class.*	H₂S is evolved : *Sulphide Dyestuff.*	No H₂S is evolved. Test ash for Cr and Cu.			
			Cr or Cu (or both) present : **Mordant Dyestuff.** Boil with HCl (1 : 20).			Cr and Cu absent : *Anthracene Vat Dyestuff,* etc.
			Completely stripped.	Not stripped or only slightly. Boil with dilute caustic soda (10 per cent.).		
				Fibre and solution dull violet.	Solution brown, fibre unaffected.	
9	10	11	12	13	14	15
Primuline developed with metaphenylenediamine, terra-cotta, etc.	Helindone brown G, ciba brown, thioindigo brown.	Immedial cutch, cross-dye brown, katigene browns, pyrogene browns, thiogene browns, etc.	Anthragallol, anthracene brown, alizarine brown.	Alizarine orange on Cr mordant, alizarine red or purpurine on Cr.	Cutch.	Indanthrene maroon, algole brown, leucole browns, cibanone brown, paramine brown (p-phenylene diamine oxidised on fibre).

Hydrosulphite BX is insufficiently acid (formation of ferrous sulphide).

TABLE

Black and Gre

Boil with w

The colour is not stripp

The colour is not stripped (or o

The colour is stripped : **Acid Dyestuff.** The dyestuff transferred to wool and boiled with Hydro-sulphite A X is permanently decolorised : *Azo Class.*	The colour is stripped.			The colour is largely stripped and the acid extract is precipitated by tannin solution : **Basic Dyestuff.** Transfer to wool and boil with Hydrosulphite A X.	
	Fibre and solution colourless.	Solution orange. Fe in ash.	Solution red. Cr in ash.	Decolorised. Colour returns on exposure to air : *Azine, Oxazine,* or *Thiazine Class.*	Colour becomes red just before being decolorised. Violet or violet blue colour returns in air : *Safranine Azo Class.*
1	2	3	4	5	6
Naphthol blacks, naphthylamine blacks, palatine black, etc.	Tannate of iron.	Logwood black on iron mordant.	Logwood black on chrome mordant, noir reduit.	Methylene grey, new methylene grey, new fast grey, nigrisine, etc.	Janus black, Janus grey, diazine grey.

Div. 1.—Chrome black (By) becomes light brown on reduction with Hydrosulphite B X and persulphates change the colo

Div. 13.—Alizarine black S (M) returns rapidly after reduction and gives the sulphide reaction with stannous chloride.

TABLE LXVII

Colours on Cotton

nd Grey

Boil with weak ammonia (1 : 100).

s not stripped. Boil with dilute hydrochloric acid (1 : 5).

ripped (or only slightly).   Boil for one minute with saline caustic soda, rinse, and boil with water and dilute hydrochloric acid (1 : 20).

A coloured acid extract precipitated by tannin is not obtained.   Reduce original fibre with Hydrosulphite B X.

Decolorised and colour not restored by air or persulphate : *Azo Class.* Boil with soap solution and white mercerised cotton.			Decolorised and colour restored by air. Gives violet vapours on heating in dry tube : *Indigoid Dyestuff.*	The colour is unaffected or changed in shade (becoming brown, maroon, etc.).				
The white cotton is stained. Test ash for Cr and Cu.		The white cotton is not stained. Colour is stripped by boiling pyridine : *Insoluble Azo Colour.*		The reduced colour is brown, but is rapidly restored to black on exposure to air : *Azine, Oxazine,* or *Thiazine Class.* Apply lead acetate test.		The reduced colour is brown. Only slowly and imperfectly restored to black by air, but at once by persulphate. Cr present in ash : *Naphthalene Mordant Dyestuff.*	Colour not changed by reduction (or very slightly) : *Anthracene Class.* Test ash for Cr.	
Cr and Cu absent : *Azo Salt Dyestuff.*	Cr or Cu present : *Azo Salt Dyestuff after-treated.*			H_2S is evolved. Fibre becomes colourless or pale buff on boiling with bleaching powder solution 5° Tw. : *Sulphide Dyestuff.*	No H_2S is evolved. Fibre becomes reddish brown on boiling with bleaching powder solution 5° Tw. : *An Oxidation Black.*		Cr present : *Anthracene Mordant Dyestuff.*	Cr absent : *Anthracene Vat Dyestuff.*
7	8	9	10	11	12	13	14	15
Blacks of the diamine, oxydiamine, benzo, Columbia, dianil, Pluto, etc., series. Also diaminogen, diazo blacks, etc. (developed or coupled).	The preceding coppered or chromed.	Azo phor black, etc.	Ciba grey G and B.	Blacks of the immedial, katigene, cross-dye, pyrogene, thiogene, thionol, pyrol, sulphur, etc., series.	Aged aniline black, prussiate black, one bath aniline black, steam aniline black, diphenyl black.	Naphthazarine S, alizarine black S, alizarine blue black S W, naphthomelane.	Alizarine cyanine black, alizarine blue black B.	Indanthrene grey, indanthrene black, cibanone black, helindone black.

ecomes before olorised r violet olour in air : ne Azo ss.

d and ed by stuff. with

e the colour loride. It

to dark brown but not to black therefore appears to fall into Div. 10.

8. Estimation of Indigo on the Fibre.—This may be effected as follows :

(*a*) ON WOOL (Green, Gardner, Lloyd and Frank's Method).[1] The indigo is extracted with pyridine at the boiling point of the solvent in Lloyd's extraction apparatus, shown in Fig. 105. This apparatus consists of an outer tube *D*, within which is a tube *A* containing the cloth or yarn to be tested. The outer tube *D* is connected at the bottom with the flask *B* charged with the solvent and at the top with an air- or water-condenser *C*. The inner tube may be of one of three forms, *a*, *b* and *c*, that best suited to the class of material to be extracted being chosen ; form *c* is most generally applicable and most commonly used. Forms *b* and *c* have glass points fused to their outer surface in order to furnish a passage for the vapour of the solvent.
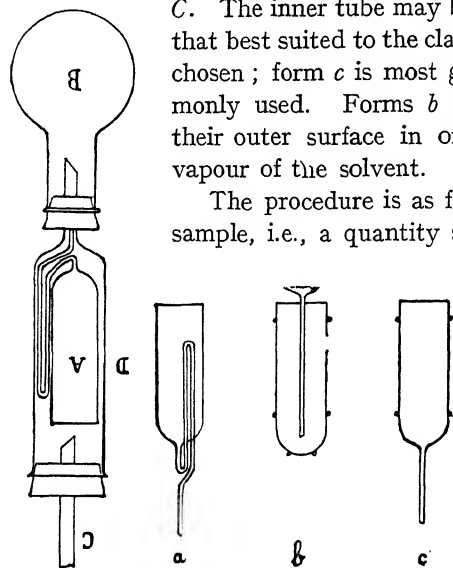
The procedure is as follows. From 3 to 15 grams of the sample, i.e., a quantity sufficient to give 0·03–0·10 gram of indigo, are packed loosely in the inner tube *A* ; with heavily felted cloth, it is advisable to cut the material into small strips or pieces. When the inner tube is of the form *c*, a little white wool or cotton wool is placed at the bottom of the tube, the material being then arranged so that the passage of the condensed solvent proceeds regularly and not too slowly or too rapidly, but in such manner that a thin layer of liquid always covers the material.

FIG. 105.

The flask *B* containing the pyridine is heated on a metal gauze or on an air-bath. The extraction is discontinued when the pyridine passes through colourless ; usually two hours are sufficient, but with thick or heavily felted goods, four hours may be required. In the latter case it is sometimes well, after an hour, to interrupt the extraction while the material in the tube *A* is rearranged.

At the end of the distillation, the pyridine extract is reduced by distillation to about 20–30 c.c. The residue is then allowed to cool, a large proportion of the indigo separating in the crystalline form with a bronze colour. The precipitation is completed by heating the mass to boiling with 100 c.c. of 50% alcohol, filtration being carried out through either a Gooch crucible charged with filter-paper or asbestos or a glass tube containing glass-wool. The filter should always be washed thoroughly beforehand with the liquids subsequently used to wash the indigo, and then dried at 110° and weighed before use. After filtration—which usually occupies only a few minutes, especially with a Gooch crucible—the indigo on the filter is washed successively with hot 50% alcohol, hot 2% caustic soda solution, hot 1% hydrochloric acid, hot water, alcohol, and lastly a mixture of alcohol and ether ;

[1] A. G. Green : *The Analysis of Dyestuffs*, 1915, pp. 79 *et seq.*

it is then dried at 110° and weighed. The purity of the indigo extracted may be judged from its appearance ; it should be a bronze-coloured, crystalline powder, and if dull is impure.

Alternatively, the indigo on the filter may be washed with cold 2% sulphuric acid, hot 10% caustic soda or ammonia, water and alcohol in succession.

The indigo may be estimated by titration instead of by direct weighing. In this case, after extraction and precipitation as above, it is collected in a Gooch crucible containing a shallow layer of asbestos. After being washed with acids and alkalies as above and dried for a short time, the crucible is placed in a small beaker containing 15–20 c.c. of pure concentrated sulphuric acid and the indigo sulphonated by leaving the beaker and its contents in an oven at 70–80° for 45 minutes. The solution is then made up to 500 c.c. and titrated in the usual way with N/50-permanganate, 100 c.c. of the indigo solution diluted with 200 c.c. of water being employed : 1 c.c. N/50-permanganate = 0·00147 gram of indigo (*see* p. 412).

The accuracy of this estimation of indigo by extracting with pyridine is not affected by the presence of other dyestuffs normally used together with indigo for dyeing woollen goods. Such dyestuffs either are not extracted, or, if extracted, are not precipitated with the indigo or are removed from the latter by washing with acid, alkali and alcohol. When, however, the indigo is accompanied—as is sometimes the case when reddish tints are desired—by certain bromindigos, these will be determined as indigo when the precipitate obtained from the pyridine extract is estimated gravimetrically. If, on the other hand, the precipitate from the pyridine extract is sulphonated and the determination carried out volumetrically with permanganate, the tetrabromindigos (ciba blue, bromindigo F B) are not sulphonated and hence remain separated.

Partly owing to their high price, other vat dyestuffs are not used either in conjunction with indigo or as substitutes for it.

(b) ON COTTON OR LINEN. Green's pyridine extraction method described above for wool may be employed for determining indigo on cotton or linen, the procedure being precisely the same.

Another method, which is more simple, is that due to Knecht [1]: Four grams of the dyed cloth, cut into small pieces, are treated in a porcelain beaker with 25 c.c. of 80% sulphuric acid (61° Baumé) and the whole kept at a temperature of about 40° and stirred until the whole of the cloth is dissolved (10–15 minutes usually suffice).

The liquid is then diluted to about 100 c.c. with water, boiled for a few minutes to render the precipitated indigo granular and filtered through a Gooch crucible containing asbestos or quartz sand covered with a layer of silica. The indigo in the crucible is washed with hot dilute ammonia and then with alcohol and, after being dried at 110–120°, is sulphonated by heating with concentrated sulphuric acid in a water-oven for an hour, and finally titrated with permanganate.

The results obtained by either of these methods of estimation are not influenced by the presence of basic, salt or sulphide dyestuffs, which are sometimes used in conjunction with indigo in dyeing cotton goods. Owing to their high price, other vat colours, with the possible exceptions of thioindigo red and bromindigos, can scarcely be used to accompany indigo. Vat colours of the

[1] *Journ. Soc. Dyers and Colourists*, 1909, pp. 135, 160.

indigoid class are extracted by pyridine and would be estimated as pyridine if weighed directly. If, however, the precipitate obtained either by pyridine extraction or by treatment of the fibre with 80% sulphuric acid is sulphonated and titrated with permanganate, only the indigo becomes soluble, whilst thio-indigo red and bromindigos remain undissolved and are not estimated.

Where indigo and another dyestuff are present, it is sometimes necessary —besides estimating the indigo—to determine the relative colour effects due to the indigo and to the other colouring matter,[1] and also to identify the latter and measure its fastness to light, washing, etc.

Identification of the concomitant dyestuff is effected in the manner indicated in paragraph 7 (p. 470), the remarks on p. 475 referring to mixtures being borne in mind. To test this dyestuff for its fastness to light, washing, etc., the indigo is first removed by means of pyridine or cresol (see p. 476) and the indigo-free cloth then examined as described in the following paragraph.

9. Fastness of Colours on the Fibre.—The fastness against light, washing, scouring, etc., of the colour on fibre is determined by the following tests and is then related to that shown by colours obtained by a definite dyeing process, use being made of the same fibre as is under examination and of a dyestuff of known chemical composition. The degrees of fastness indicated in the different tests are sometimes five and sometimes as many as eight and are denoted by Roman numerals, I representing the least and VIII the greatest fastness.

As regards the typical shades corresponding with the different degrees of fastness for each test, and their method of preparation, agreements have been arrived at between industrial associations and manufacturers of dyestuffs with the object of unifying the criteria determining the fastness of dyed and printed materials.

The tests to be made are as follows:

(a) ON COTTON.

1. *Fastness against light.* These tests should be made both under glass and in the open air and are always relative to the duration of the exposure and to the season in which they are made.

The test under glass is carried out in the following manner: A piece of the material is stretched on a wooden frame and covered with cardboard which is white on the upper face and black on that in contact with the sample and has a central hole about 8 cm. in diameter. The card is covered with glass and the whole exposed to the light in the open air but protected from the weather.

For the open-air test a piece of the material is covered to the extent of one-half with black paper and exposed to the light in a place protected from the weather.

In both cases observations are made on the samples every seven or eight days for a month, the uncovered and covered parts being compared.

Tests made simultaneously and under the same conditions with cottons dyed by means of the typical dyestuffs referred to above will indicate to which of the eight degrees of fastness the colour of the sample approximates. Comparison may also be made with an agreed sample.

2. *Fastness against washing and boiling of the dyed cotton relative to white*

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[1] A. G. Green: *The Analysis of Dyestuffs*, 1915, pp. 85 et seq.

cotton. (*a*) The sample, mingled with an equal quantity of white cotton yarn, is treated for half an hour in a bath (50 times the weight of the sample) of Marseilles soap (2 grams per litre) at 40° C. It is then removed from the bath, rubbed between the fingers and returned to the bath, this procedure being repeated ten times; it is finally washed and dried. The degrees of fastness are classified as follows: I, the tint becomes a little paler, and the white cotton is coloured; II, tint unaltered, white cotton coloured but little or not at all.

(*b*) The sample, mixed with an equal quantity of white cotton yarn, is boiled for half an hour in a solution of 3 grams of Marseilles soap and 3 grams of calcined soda per litre; the bath is then cooled to 40° and the sample left in it for a further 30 minutes and subsequently treated as in (*a*). The degrees of fastness to this treatment are classified as follows: III, the shade becomes slightly paler, the white cotton is only feebly coloured; IV, the shade remains unchanged, the white cotton is only slightly coloured; V, the shade remains unchanged, and the white cotton remains white.

3. *Fastness against water.* The sample is mixed with white cotton yarn, washed zephyr wool and white silk, one part of white material being taken to two parts of coloured. It is then immersed for an hour in distilled water (40 times the weight of the sample) at 20° C., and afterwards wrung out and dried. The degrees of fastness are as follows: I (with a single treatment), shade lightened, white coloured; III (with a single treatment), shade and white unchanged; V (with three consecutive treatments), shade and white unchanged.

4. *Fastness against scouring.* The sample is rubbed ten times up and down energetically with a piece of white cotton materal stretched between the fingers to ascertain if the white cotton becomes coloured and to what extent. No standards are fixed for this test.

5. *Fastness against ironing.* The sample is covered with a fine undressed white cotton fabric moistened with distilled water, and ironed with a hot iron until the cotton is dry. The iron should be so hot that it causes a woollen material to burn slightly. The degrees of fastness are classified as follows: I, tint altered, white cotton coloured; III, tint somewhat changed, white cotton untouched; V, tint and white cotton unchanged.

6. *Fastness against sulphur.* The sample is mixed with washed white zephyr wool, washed with a solution of 5 grams of Marseilles soap in a litre of water, wrung out and left for 12 hours in an atmosphere of sulphur dioxlde obtained by burning excess of sulphur. The degrees of fastness in this test are classified thus: I, tint unchanged, white dyed; III, tint slightly changed, white unaltered; V, tint and white unchanged.

7. *Fastness against perspiration.* The sample is mixed with an equal quantity of white, cotton yarn, left for 10 minutes in a solution containing 5 grams of neutral ammonium acetate in 5 litres of distilled water at 80° C., and subsequently dried without rinsing. The degrees of fastness towards this treatment are thus classified: I, tint paler, white highly coloured; III, tint unchanged, white coloured; V, tint and white unchanged.

8. *Fastness against alkalies* (*dust and mud*). The sample is steeped in a liquid containing 10 grams of quicklime and 10 grams of 24% ammonia in a litre of water, and afterwards wrung out and dried without washing. The degrees of fastness in this test are : I, colour considerably changed ; III, colour somewhat changed ; V, colour unchanged.

9. *Fastness against acids*. The sample is soaked in 10% sulphuric acid or in 30% acetic acid and the colours compared with that of a sample soaked in water. The degrees of fastness are as follows : I, alteration marked with mineral acids, weak with organic acids ; III, alteration marked with mineral acids, absent with organic acids ; V, no alteration with either mineral or organic acids.

10. *Fastness against bleach.* The sample is mixed with an equal quantity of white cotton yarn, washed in hot water and then left for an hour in a fresh bath of calcium hypochlorite containing 0·1% of active chlorine or in a sodium hypochlorite solution containing 1 gram of active chlorine and 0·3 grams of soda per litre. The material is then rinsed, acidified, washed, wrung out and dried. The recognised degrees of fastness are as follows : I, with sodium hypochlorite : colour paler, white coloured ; with calcium hypochlorite : colour much paler, white coloured ; II, with sodium hypochlorite : colour altered, white unaltered ; with calcium hypochlorite : colour profoundly altered, white unaltered ; III, colour altered (much more with calcium hypochlorite), white unaltered ; IV, white unaltered, colour paler only with calcium hypochlorite ; V, colour and white unchanged.

11. *Fastness against mercerisation.* The sample is boiled with undressed bleached cotton, then immersed for 5 minutes in cold caustic soda solution (30° Baumé), washed, acidified, washed thoroughly and dried. The degrees of fastness are : I, colour slightly changed, white somewhat coloured ; III, colour unchanged, white slightly coloured ; V, colour and white unaltered.

With dyed linen, hemp, ramie and jute materials, there are no such precise standards of fastness as for cotton. In general, however, linen, hemp and ramie products are examined, in the manner described above, by most of the tests indicated for cotton materials. Goods made of jute are usually only tested to ascertain if they withstand the action of water without losing their colour.

(*b*) On Wool.

1. *Fastness against light.* This is tested as with cotton, and there are eight degrees of fastness.

2. *Fastness against washing of dyed wool with respect to wool and to cotton.* This test is carried out in two ways : (*a*) The sample is mixed with equal amounts of washed white zephyr wool and of washed white cotton and treated for 15 minutes at 40° in a bath (50 times the weight of the sample) containing per litre 10 grams of perfectly neutral Marseilles soap and 0·5 gram of calcined sodium carbonate ; it is then wrung out by hand and rinsed ; (*b*) The procedure given in (*a*) is followed but a temperature of 80° employed.

The degrees of fastness with respect to wool in this test are classified as follows : I (treatment *a*), marked alteration of the colour, white wool strongly coloured ; II (treatment *a*), no alteration of the colour, white not

coloured; V (treatment *b*), no alteration of the colour, white coloured little or not at all. The degrees of fastness with respect to cotton in this test are: I (treatment *a*), the white cotton is deeply coloured; III (treatment *a*), white not coloured; V (treatment *b*), white not coloured.

3. *Fastness against water.* This test is carried out as with dyed cotton fabrics, but the immersion is extended to 12 hours. The degrees of fastness are as follows: I (with one treatment), colour weakened, white coloured; III (with one treatment), colour and white unchanged; V (with three treatments), colour and white unchanged.

4. *Fastness against scouring.* As with cotton.

5. *Fastness against ironing.* The sample is pressed for 10 seconds with a hot iron, the temperature of the latter being such that it does not begin to burn a piece of woollen material when passed over it. The degrees of fastness in this test are: I, colour greatly altered, the original colour returning only gradually or incompletely; III, colour somewhat altered, the original colour returning rapidly on cooling; V, no alteration.

6. *Fastness against sulphur.* This test is carried out as with cotton. The degrees of fastness are classified thus: I, colour somewhat altered, white slightly coloured; III, colour slightly changed, white intact; V, colour and white unchanged.

7. *Fastness against perspiration.* This test is carried out in two ways: (*a*) The material is dipped into a solution of 10 grams of common salt in distilled water and then left to dry at the ordinary temperature, the degrees of fastness with reference to this treatment being: I, colour greatly altered; III, colour somewhat altered; V, no change.

(*b*) As with cotton the test may be made with ammonium acetate, the sample being, however, mixed with equal quantities of white zephyr wool and white cotton. The degrees of fastness with reference to this test are classified thus: I, colour at the most slightly altered, cotton and wool coloured; III, colour and cotton unchanged, wool slightly coloured; V, colour, wool and cotton unchanged.

8. *Fastness against alkalies* (*dust and mud*). As with cotton. The degrees of fastness are: I, marked alteration; III, colour somewhat altered; V, no alteration.

9. *Fastness against boiling with acids.* The sample is mixed with white zephyr wool, treated for $1\frac{1}{2}$ hour in a bath (70 times the weight of the sample) consisting of a 0·25% solution of sodium bisulphate in distilled water, and then washed and dried. The degrees of fastness are classified as follows: I, coloured slightly altered, white coloured; III, colour unchanged, white little coloured; V, colour and white unchanged.

10. *Fastness against milling.* (*a*) Neutral milling: The sample is made into a skein with an equal quantity of white wool or cotton and treated at 30° C. in a bath (40 times the weight of the sample) containing 20 grams of Marseilles soap per litre of distilled water; it is scoured with the hands in the liquid, left in the bath for 2 hours, washed and dried.

(*b*) Alkaline milling: The treatment is as in (*a*) but at 40° C. and in a bath containing 20 grams of Marseilles soap and 5 grams of Solvay soda per litre of distilled water.

The degrees of fastness in this test are classified as follows : With respect to white wool : I (treatment *a*), colour unaltered, wool coloured ; II (treatment *a*), slight alteration of the colour, wool dyed ; III (treatment *a*), colour very slightly or not at all altered, white unaltered ; IV (treatment *b*), no alteration of the colour, white slightly coloured ; V (treatment *b*), no alteration of the colour or of the white. With respect to white cotton : I (treatment *a*), white cotton strongly coloured ; II (treatment *a*), white cotton slightly coloured ; III (treatment *a*), white cotton not coloured ; IV (treatment *b*), white cotton very slightly coloured ; V (treatment *b*), white cotton not coloured.

11. *Fastness against carbonisation.* The sample is left for half an hour in sulphuric acid of 5° Baumé, wrung out and dried for an hour at 80° C. It is then either washed for 15 minutes with 200 times its weight of distilled water and wrung out, or treated for 15 minutes with 0·2% sodium carbonate solution and subsequently thoroughly washed. The degrees of fastness in this test are classified thus : I, colour altered considerably ; III, slight alteration of the colour ; IV, no alteration of the colour.

12. *Fastness against sea-water.* The sample is made into a skein with an equal quantity of white wool and left immersed for 24 hours in a bath containing 30 grams of common salt and 6 grams of calcium chloride per litre. The degrees of fastness in this test are : I, colour slightly altered, white strongly coloured ; III, colour very slightly altered, white slightly coloured ; V, colour and white unchanged.

(*c*) ON SILK. With silk no precise data exist for investigating the fastness of the colour. The following tests are usually made with dyed silk goods :

1. *Fastness against light.* As with cotton.

2. *Fastness against water.* The dry dyed silk is kept immersed for some days in distilled water to ascertain if the colour undergoes alteration.

3. *Fastness against soap.* The dyed silk is made into a skein with white linen or cotton, then immersed for 10 minutes in a soap bath (10–15 grams of white Marseilles soap per litre) heated to 40–45° C., washed in running water and dried.

4. *Fastness against acids.* This test is made with a bath containing 1 c.c. of concentrated sulphuric acid per litre of water, heated first to about 40° and then to boiling for half an hour.

5. *Fastness against finishing.* This test is applied to those fabrics which are to be subjected to calendering in the hot or to gassing to burn off the down. The sample is either passed four or five times over a flame, or drawn slowly across the surface of a tube inside which steam passes, to ascertain if any change occurs in the colour of the fabric.

10. Nature of Waterproofing.—Cloths are rendered waterproof or impervious in various ways :

(*a*) By imbibition of fatty, oily or tarry substances (oiled or tarred fabrics), or the like.

(*b*) By immersion in a suitable bath leading, after special treatment, to the formation of insoluble compounds on the elements composing the material, the latter being thus rendered waterproof or impermeable (alu-

minium or copper acetate, aluminium tannate; fatty or resin soaps of aluminium, copper or iron; fatty acids).

(c) By coating one or both sides of the material with a layer of rubber or by uniting two fabrics by means of a layer of rubber.

(d) By covering one or both faces with a layer of pasty material, which is capable of drying rapidly and is based on waxy or paraffin materials or drying oils; the most diverse mixtures of these substances with rubber, resin, castor oil, gypsum, barium sulphate, kaolin, talc, ferric oxide, lamp black, etc. (waxed cloth, etc.), are also used.

(e) By covering one or both faces of a material with a more or less thick, uniform layer of nitrocellulose and camphor mixed sometimes with castor oil and with coal-tar colouring matters or substances which give it an opaque appearance, such as zinc oxide, mineral white (pegamoid fabrics, etc.).

In investigating waterproofing, attention should first be paid to the external characters of the material. If treated by any of the processes referred to in (a) or (b), the fabric shows more or less clearly the warp and woof threads constituting it and also their interweaving. If, however, the impermeability is obtained by the processes referred to in (c), (d) or (e), the coating on one or both sides will conceal the threads making up the fabric and consequently also their interweaving. The only apparent exceptions are waterproof fabrics prepared by superposition of two materials held together by a layer of rubber. Besides the appearance, the smell also may serve to indicate the nature of the waterproofing; thus, rubbered fabrics smell of rubber and tarred materials of tar, and, if recently made, pegamoid materials smell of camphor, especially if rubbed between the fingers.

In the chemical examination, the following cases are distinguished:

1. FABRICS IN WHICH THE SEPARATE THREADS AND THEIR INTERWEAVING REMAIN VISIBLE (oiled, tarred, impregnated with wool-fat or fatty acids, treated with aluminium or copper acetate or aluminium tannate, aluminium, copper, or iron soap or resinate).

(a) A piece of the material is boiled in a reflux apparatus successively with ether, carbon tetrachloride, benzene, and alcohol, the treatment being stopped when the waterproofing material passes into solution in one of the solvents. This may be tested by ascertaining if the material treated in this way and well dried in the air has lost its impermeability totally or in part, and also by evaporating the extract in a porcelain dish on a water-bath and examining the residue; the latter should consist of oil or fat, tar or fatty acids.

(b) If the above tests give negative results, another piece of the fabric is incinerated, the colour and chemical composition of the ash serving to indicate the presence in it of any appreciable quantities of aluminium, copper or iron. Another piece of the material is then boiled with ether acidified with hydrochloric acid, the acid liquid thus obtained being placed in a separating funnel and the acid and ethereal layers collected apart. The former may be used to confirm the presence of aluminium, copper or iron if such were found previously in the ash, while the latter is evaporated in a porcelain dish on a water-bath and any residue thus obtained examined

to ascertain if it consists of fatty acids or resin or tannin. If both tests give positive results, it may be concluded that impermeability is obtained with aluminium, copper or iron soap or resinate, or aluminium tannate. If both the ash and the acid liquid show the presence of copper or aluminium and evaporation of the ethereal layer gives no appreciable residue, the conclusion may be drawn that the impermeability is based on aluminium or copper acetate. In both cases the fabric treated as described above loses part or the whole of its impermeability.

2. FABRICS COVERED ON ONE OR BOTH FACES WITH A LAYER WHICH CONCEALS THE THREADS AND THE WEAVING (rubber, pegamoid, markedly drying oils).

(*a*) Rubbered fabrics exhibit a characteristic odour and appearance which alone suffice for their identification. The rubber may be removed —so that the fibres may be identified or estimated—by immersing the material for about an hour in a mixture of equal volumes of benzene and oil of turpentine on a water-bath. The rubber is thus softened and swollen and may be removed readily by scraping with a knife. The removal may be completed by dipping the fabric repeatedly into the hot solvent and renewing the latter from time to time.

(*b*) To confirm the presence of pegamoid—which is indicated by the appearance and smell—the following methods are used:

1. Undyed pegamoid fabrics are treated with a few drops of concentrated sulphuric acid containing a small quantity of diphenylamine in solution: a blue spot is formed (reaction of nitro-compounds).

2. With dyed pegamoid fabrics these tests may be applied:

According to Perrin,[1] a piece of the fabric is boiled in a reflux apparatus with 30–40 c.c. of ethyl acetate, the liquid being then filtered and treated with 4–5 times its volume of chloroform. The flocculent nitrocellulose thus precipitated is filtered off and identified by its mode of burning and by the blue coloration it gives with sulphuric acid and diphenylamine. The ether-chloroform liquid may be examined for fatty oil (usually castor oil); insoluble mineral substances may be analysed separately. When treated in the above way, some forms of pegamoided fabrics give no precipitate with chloroform, but in this case evaporation of the ethereal chloroform liquid would yield a residue consisting of a shining pellicle of nitrocellulose, which burns rapidly if brought into contact with a flame.

When a piece of pegamoided fabric is immersed for some time in a mixture of alcohol and ether, the coating of pegamoid becomes detached and passes into solution with the exception of the mineral substances, which are deposited on the bottom of the vessel. Evaporation of the filtered alcoholic ethereal liquid gives a shining skin of nitrocellulose, which burns rapidly.

(*c*) The so-called waxed fabrics now sold consist almost entirely of vegetable fibres coated with oils with marked drying properties, usually mixed with mineral substances; such materials exhibit the odour of oily substances. This oily layer is removable, not by the ordinary solvents, but by boiling 10% caustic soda solution and alcohol. Acidification with

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[1] *Monit. scientif.*, 1898, p. 876.

hydrochloric acid of the alkaline liquid thus obtained liberates the fatty acids, which may be extracted with ether in a separating funnel. If the ethereal layer is filtered, the mineral matter used for weighting or colouring remains on the filter and evaporation of the filtrate in a porcelain dish on the water-bath yields a residue of the fatty acids.

11. Investigation of the Waterproofing Qualities.—The efficiency of the waterproofing may be tested as follows :

(a) BAG TEST. A square of the material, free from defects, is tied with string by the four corners to a wooden frame so as to make a kind of bag, into which water is poured to a depth depending on the uses to which the fabric is to be put. With certain cloths the greatest depth is taken as 75 mm., whilst with fabrics for tents and sails a depth of 100 mm. is usually employed. The test mostly lasts 24 hours, during which time, if the fabric is quite impermeable, the water should not drip through. Mere transudation of the water to the lower surface of the fabric in 24 hours is not sufficient to indicate poor waterproofing. Sometimes the material is allowed to dry after the first test and is then subjected to a second and even a third test.

(b) FUNNEL TEST. When the amount of the fabric available is insufficient for the above test, a piece of it is placed in a glass funnel like a filter-paper and water poured on to it and left for 24 hours.

(c) BURETTE TEST. One end of a graduated glass tube of the diameter of an ordinary burette is completely closed by a piece of the material and 10, 20 or 30 c.c. of water, according to circumstances, poured into the tube ; the other end of the tube is covered and any water which passes through the fabric in 24 hours measured.

The results obtained in each of these three tests are related to the depth of water above the fabric—this determining a certain pressure on the latter [1]—and to the temperature of the water and of the surrounding air.

(d) SPRAY TEST. In some cases it is useful to know the impermeability of a fabric exposed to rain, that is, either what time elapses before water passes through the fabric or if the latter resists the rain for some definite time. This test may be made as follows : A piece of the sample is stretched over a cubical vessel of 40 cm. side (dry inside) so as to prevent infiltration of water except through the material. The vessel is inclined at 25° and a spray of water (3 litres per minute) dropped for 3 hours from a height of 2 metres on to the central part of the fabric so as to cover an area about 30 cm. in circumference. At the end of the experiment, no water, or at most a minimal quantity, should have traversed the material.

Apparatus has been devised to render easier determination of the degree of impermeability of fabrics to still water, rain and air.[2]

12. Degree of Imbibition.—A square decimetre of the material is left for 12 hours in a space with a relative hygroscopicity of 65° and afterwards weighed. It is then suspended by one corner and a weight of 20

[1] As regards tests for the impermeability to water of fabrics under pressure, *see* P. Heermann : *Mechanisch und physikalisch-technische Textil-Untersuchungen*, Berlin, 1912, p. 235.
[2] *See* G. A. Le Roy : "L'expertise de l'imperméabilisation des tissus," *Annales des Falsifications*, Nos. 85 and 86, November and December, 1915.

grams hung at the opposite corner. It is next immersed in a water-bath at 18° C. and at the end of a definite time, say 5–10 minutes, raised above the surface of the liquid and allowed to drip with the weight removed for exactly 15 minutes and weighed. The percentage increase of weight represents the power of imbibition relative to the conditions of the test.

In some cases the imbibition test is made by exposing a square of half-metre side—weighed after 12 hours in a medium with a relative humidity of 65°—to a water-spray in the manner described on p. 521 (*d*). After draining for 15 minutes as above, the fabric is weighed and the percentage increase calculated.

13. Investigation and Estimation of the Weighting of Silk.— Ordinary silk is loaded with dressing and colouring matter, sometimes in considerable quantities, in order to increase the weight, such addition of extraneous substances being termed the " weighting " of silk.

The more usual weighting materials to be tested for are : stannic oxide either free or combined with phosphoric acid or silica ; ferric oxide either free or combined with cyanogen or tannin ; oxides or salts of aluminium, zinc and magnesium ; also, although less common, tungstic acid and its salts, barium sulphate, lead and antimony salts, chromium oxide, etc. With some silks use is made of starchy materials, dextrin, glucose, glycerine, oily substances and the like, which form not so much a true weighting as a kind of dressing and are sometimes applied with the view of beautifying the silk and rendering it softer to the touch.

QUALITATIVE INVESTIGATION OF THE NATURE OF THE WEIGHTING. The following tests are made :

The dry fabric is exhausted first with ether or petroleum ether, the extract being tested for fatty substances. It is then heated with water, which removes any glucose, glycerine, dextrin, gum, soluble metallic salts (calcium chloride, magnesium sulphate, potassium sulphate) and partly also glue, starch and certain lead salts contained in the weighting ; the aqueous solution is tested by the ordinary methods for these substances. The fabric is then heated to about 40° with 2% sodium carbonate solution ; this dissolves the tannin substances, glue, small quantities of antimony and tin and part of the tungstic acid and also attacks Prussian blue ; tannin is identified by neutralising the solution and adding a ferric salt (brown coloration), and Prussian blue by acidifying the solution and adding ferric chloride (blue precipitate). The residual fabric is heated to about 60° with 5% hydrochloric acid, which removes part of the salts of tin, iron (not as Prussian blue) and aluminium, and also any other tannin and phosphates. Incineration of the residual matter gives an ash containing the silicates and also part of those metals, especially tin and antimony, not completely removed by the previous treatment.

QUANTITATIVE DETERMINATION OF THE WEIGHTING. As weighting is regarded only the excess of weight of the weighted product over that in the raw state, disregarding the 7–8% which the silk loses during softening and the 20–25% which it loses during boiling or stripping.

The methods for the quantitative determination of the weighting are various and are based on :

(a) The determination of the weight of the silk.

(b) The determination of the nitrogen.

(c) The extraction of the weighting substances.

(d) The determination of the weight of the ash.

As regards the sample, J. Persoz [1] recommends that it be weighed after being left for some time in a dry space. When method (c) is used, the silk free from weighting should be weighed after it has been dried in the room in which it remained before being weighed originally.

(a) *Method based on the weight of the silk.* If the count (t) of the raw silk thread yielding the silk of count T is known, the percentage of weighting (C) is given by :

$$C = \frac{100 \ (T - t)}{t}.$$

In other cases 10 metres of the silk are weighed [2] to within a milligram and the weight divided by 10, this giving the weight of 1 metre in milligrams. Ten pieces of the silk are then examined under a lens or microscope to ascertain of how many filaments they consist, the mean (n) being taken.

Then $\frac{p}{n} = p'$ is the weight in milligrams of 1 metre of filament as it occurs in the sample.

The difference between this weight p' and that of a metre of the raw silk fibre [3] will give the weighting.

This method is very rapid and simple, but the origin of the silk must be known. The results obtained differ, according to Ristenpart, from the real weighting of the product by as much as 20%. The method is, consequently, to be followed only when small amounts of the silk are available and approximate results are sufficient.

EXAMPLE : 1 metre of the fibre of an Italian organsine (p') is found to weigh 0·400 mgrm. :

$$0·400 - 0·160 = 0·240$$

Weighting = 240/160 = 150%.

(b) *Method based on the determination of the nitrogen.* This method consists in removing from the silk the extraneous substances, which might contain nitrogen, and then determining the nitrogen content of the silk thus treated. From the amount of nitrogen that of the fibroin is calculated and hence that of the raw silk, the weighting being determined by difference. The procedure is as follows [4] :

From 1 to 2 grams of the silk are boiled for 10 minutes in 25% acetic

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[1] *Revue générale des matières colorantes*, 1906, p. 326.

[2] Ristenpart : " Kritische Studien zur Analyse der Seidenerschwerung '' (*Färber Zeitung,* 1907, p. 298) ; Gianoli and Zappa : " Determinazione del titolo che una seta tinta presentava allo stato greggio " (*Industria,* 1900, p. 268).

[3] According to Ristenpart, the mean weight of a metre of raw silk fibre may be taken as :

For Italian or Japanese organsine,	0·160 mgrm.	
For ,, ,,	tram,	0·150	,,
For Canton	organsine,	0·102	,,
For ,,	tram,	0·088	,,
For Chinese	organsine,	0·111	,,

[4] Sisley : *Revue générale des matières colorantes,* 1907, p. 97.

acid, the liquid being then decanted and the residue washed with distilled water. The silk is then immersed for 10 minutes in a 3% solution of crystallised trisodium phosphate [1] kept at 50° C., the liquid being decanted and the residue washed with distilled water. The silk is then treated for 20 minutes in a boiling 3% soap solution containing 0.2% of anhydrous sodium carbonate. This last treatment is repeated and the silk then washed with distilled water and dried.

With silk which has undergone change, the sample is enclosed in a little bag of cotton cambric—to avoid losses—and then subjected to the above treatment, the Kjeldahl process being subsequently carried out on the bag containing the treated silk; 20 c.c. of concentrated sulphuric acid, 10 grams of pure potassium sulphate and 0.5 gram of dried copper sulphate are used (see Vol. I, p. 122), complete decolorisation requiring about half an hour.

The mean nitrogen content of dry ungummed silk is 18.4%; in practice, however, the weighting is referred to the moist silk, so that the nitrogen content must also be calculated for silk with the normal moisture (11%), the value being thus 16.38%. Consequently, one part of nitrogen corresponds with 6.105 parts of ungummed silk with its normal moisture.

When there is no indication of the loss undergone during the ungumming of the silk prior to weighting, such loss is usually taken at 25% for organsine and 20% for tram silk, so that with 75 or 80 parts of fibroin found there correspond 25 or 20 parts of sericin.

EXAMPLE :

1 gram of organsine gave 0.067 gram of nitrogen ;
$$0.067 \times 6.105 = 0.409035 \text{ gram of moist ungummed silk.}$$
If the loss on stripping is assumed to be 25%, the amount of sericin corresponding with this amount of ungummed silk will be
$$\frac{0.409035 \times 25}{75} = 0.136345.$$
The weight of the moist organsine before ungumming is hence
$$0.409035 + 0.136345 = 0.54538 \text{ gram.}$$
The weighting corresponding with 1 gram of the silk under examination is
$1 - 0.54538 = 0.45462$ gram and the percentage weighting will be
$$\frac{0.45462 \times 100}{0.54538} = 83.35.$$

In place of the treatment with acetic acid, sodium phosphate, soap and sodium carbonate proposed by Sisley for the removal of extraneous nitrogenous substances, G. Gianoli [2] suggests the treatment of 1–2 grams of the silk for 10 minutes at 50° C. with a 2% caustic soda solution containing 4.5% of glucose. The silk is then washed and dried, and the nitrogen estimated by the Kjeldahl method—the silk being boiled for 5 minutes in 20 c.c. of concentrated sulphuric acid.

The above method of determining the weighting—based on the estimation of the nitrogen in the fibroin—is applicable to silks of all qualities and gives good results.

(c) *Methods in which the weighting substances are extracted.* The following different cases are distinguished :

[1] Treatment with trisodium phosphate is necessary only for black silks.
[2] *L'Industria*, 1907, p. 540.

1. Weighting soluble in water : When qualitative tests indicate the silk to be weighted with sugar, glucose, or salts or other substances soluble in water, the weighting is estimated by extracting with water a known weight of the " conditioned " silk and reweighing it after drying it and conditioning it again.

2. Tannin weighting : When weighting has been obtained solely with tannin materials without mineral salts, Sisley [1] recommends the following method : 1–2 grams of the conditioned silk are boiled with three successive quantities of 200 c.c. of distilled water, each time for 5 minutes, then twice with 200 c.c. of 20% acetic acid (5 minutes each time), and after being washed with distilled water and faintly ammoniacal water, twice with 200 c.c. of 3% soap solution containing 0·2% of sodium carbonate (20 minutes each time). The silk is afterwards washed successively with faintly ammoniacal water and distilled water alone, the excess of water being wrung out and the sample dried in an oven and conditioned. The weight then represents the ungummed silk, free from weighting, contained in the sample taken.

Silks treated in the manner indicated are usually slightly coloured and still contain minute proportions of tannin, but these do not exceed 0·5% and may be neglected.

3. Mixed weighting based on tannin and mineral substances : For either white or coloured silk, the following method may be adopted.[2] The weighed sample is moistened and immersed for an hour in a cold 10% hydrofluoric acid solution (6·9° Baumé) in a copper vessel, a copper rod being used for stirring. The silk is then washed ten times with distilled water and afterwards immersed for 5 minutes in a cold normal caustic potash solution. After five washings with distilled water slightly acidified with acetic acid, the silk is washed five times with water, wrung out, allowed to dry at the ordinary temperature and weighed. This weight represents the ungummed silk free from weighting contained in the sample. To calculate the percentage of weighting imparted to the silk when the loss on ungumming is unknown, such loss is taken as 25% for organsine and as 20% for tram silk.

EXAMPLE : 3·45 grams of boiled and weighted silk, after the treatment indicated, leave 1·35 gram of ungummed silk. The original weight of raw organsine is given by :

$$75 : 25 :: 1·35 : x, \text{ so that } x = 0·45$$
$$1·35 + 0·45 = 1·80 \text{ (original weight of raw organsine)}$$
$$3·45 - 1·80 = 1·65 = \text{weighting}$$
$$1·80 : 1·65 :: 100 : x$$
$$\text{Thus } x = 91·6\%.$$

The results obtained are always a little low and should be increased by about 5%.

For black silk and especially for silks dyed with monopol black (on tin and catechu), the following method may be used [3] :

The weighed and wetted sample is immersed for an hour in cold 10%

[1] *Revue générale des matières colorantes*, 1907, p. 99.
[2] Ristenpart : *Färber Zeitung*, 1907, p. 297.
[3] Ristenpart : *Färber Zeitung*, 1908, p. 53.

hydrochloric acid (6·6° Baumé), then washed with distilled water and left for 5 minutes in a cold normal caustic potash solution.[1]   It is then well washed ten times with distilled water and the treatment with hydrochloric acid and caustic potash repeated.   After being washed, it is allowed to dry and weighed, the calculation being made as with coloured silk.

The weight obtained represents directly the ungummed silk without weighting if the silk were originally ungummed and then weighted and if the weighting were carried out recently.

With boiled silk which has been dyed for some time with monopol black or when the latter has been applied to raw silk, the above method removes the organic weighting completely but not the mineral weighting.   In such cases and in general whenever the condition of the silk before dyeing or when the latter was effected is unknown, Ristenpart recommends that the sample treated in the above manner be incinerated, the weight of the ash being multiplied by 1·4 and this product subtracted from the weight of the sample after treatment with hydrochloric acid and caustic potash.

EXAMPLE: 2·751 grams of tram silk, after treatment with HCl and KOH are reduced to 1·254 gram, this yielding 0·185 gram of ash.   Thus,

$$0·185 \times 1·4 = 0·259 \text{ gram}$$
$$1·254 - 0·259 = 0·995 \text{ gram of ungummed silk}$$
$$80 : 20 :: 0·995 : 0·2487$$
$$0·9950 + 0·2487 = 1·2437 = \text{raw silk}$$
$$2·751 - 1·2437 = 1·5073 = \text{weighting}$$
$$1·2437 : 1·5073 :: 100 : 121$$

The weighting of the silk is hence 121%.

(d) *Method based on incineration.*   For white or pale silks weighted with silico-phosphate of tin or with silico-phosphate of tin and aluminium, P. Sisley[2] recommends that a known weight of the silk be incinerated, the weight of the ash, multiplied by 1·28, representing the weighting of the sample.   In the way described in the preceding examples, the weight of the raw silk corresponding with that of the silk taken is calculated and then the weighting referred to 100 parts of the raw silk.

14. Distinction between Raw and Bleached Products.—In the raw state, many textile fibres, such as flax, hemp, jute, etc., exhibit a colour quite distinct from white and in these cases the distinction between raw and bleached products is simple and is made by the eye.   Other fibres, however, such as those of cotton and wool, are often white in the unbleached state and in such cases the distinction between the raw and bleached products cannot be made by the eye but requires investigation.

(a) COTTON.   A practical method is as follows[3]:

The yarn or a few isolated threads of the fabric—either woof or warp —are carefully defibred with a knife ; with twisted threads it is well, before defibring, to decompose them into the simple threads.

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[1] In place of the treatment with normal caustic potash, which might attack the fibre in the case of silk which is only slightly resistant, Heermann advises treatment in a water-bath at 80° for 10 minutes with a mixture of equal volumes of glycerine and 2 N-caustic potash, the silk being left in this liquid for a further 5–10 minutes after its removal from the water-bath.

[2] *Revue générale des matières colorantes,* 1907, p. 102.

A. Cappelli : *Ann. Labor. chim. centrale Gabelle,* Vol. VII, p. 225.

The fibres thus obtained, after removal of the knots and pieces not well defibred, are grouped so as to make a roughly circular tuft about 1 cm. in diameter and 1 mm. thick. This tuft is placed on the surface of distilled water contained in a weighing bottle and observed during a period of a few minutes. With raw products, the tuft of fibres does not become wetted and remains floating even when the liquid is agitated; with a bleached product, on the other hand, the tuft is wetted more or less rapidly and, when the liquid is shaken, falls slowly to the bottom.

When dressed products are to be examined, a small portion is washed for about 15 minutes under the tap and rubbed vigorously between the fingers meanwhile; it is then allowed to dry completely in the air and afterwards tested as above.

Thread of the sewing cotton type should be scraped with a knife to remove the dressing and then kept for about 30 minutes in distilled water on the water-bath, the water being changed two or three times. It is next allowed to dry in the air, broken up into its constituent simple threads and the latter defibred, the fibres obtained being tested as above.

(b) WOOL. If the bleaching were effected by means of sulphurous anhydride, the following method may be used[1]: A few pieces of thread taken from the sample, and if twisted, split up into the separate fibres composing them, are tied in a small bundle with a simple knot in the middle and placed in a porcelain dish. On to it is then poured a little of the following iodine reagent, recently prepared: 1 gram of sublimed iodine and 5 grams of potassium iodide are dissolved in about 50 c.c. of distilled water and the solution made up to a litre with distilled water.

With the help of a glass rod the fibres are completely wetted with the reagent, the bundle being then removed, well drained and separated into the component threads, which are spread out on absorbent paper.

By this treatment all woollen fibres are coloured a more or less intense yellow. On exposure to the air, however, fibres which have been bleached soon begin to turn paler and after a few minutes (usually not more than 15) become colourless or white again, whereas raw fibres which have not been treated with sulphurous anhydride retain an intense yellow coloration even after an hour. Fibres which have been incompletely bleached (milk white, ivory white) retain the yellow colour of the iodine, although in less intensity, for some minutes, but after an hour they are almost always colourless, or only pale canary-yellow.

The test should always be carried out on the single fibres and without previously subjecting them to any preliminary treatment with water or other chemical reagents.

Where other bleaching agents, such as hydrogen peroxide, permanganate and the like, have been used instead of sulphur dioxide, the test is inapplicable.

Washed linen and hempen goods are also sold which have been subjected to intermediate treatment to the raw and the bleached products, and it may sometimes be necessary to distinguish such washed goods from the corresponding raw materials. A simple method of differentiation is based on comparison of

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[1] A. Solaro: *Ann. Labor. chim. centr. Gabelle*, Vol. VI, pp. 4 7 *et seq.*

the colour of the aqueous extract of the product in question with that given under the same experimental conditions by the same weight of undoubtedly raw linen or hemp thread or cloth ; before comparison, the two extracts are made up to equal volumes. The comparison may be made in fairly large, similar test-tubes. Washed products give solutions much less yellowish-brown than the corresponding raw products.

3. Physico-mechanical Examination

This examination includes numerous technical tests and investigations made with the object of determining the physico-mechanical properties of the wares. The results obtained, together with those of the microscopic and chemical examinations, indicate if the material possesses the necessary characters for the required purpose and also allow of its value being established. This examination is carried out on a sample so chosen that it represents as far as possible the whole parcel. The tests made are numerous and only a few of the more important are given shortly here ; further details may be found in special books on the subject.[1]

1. APPEARANCE AND EXTERNAL CHARACTERS. These include the colour, smell, purity, degree of softness and uniformity of the sample, the presence of any obvious defects of treatment (spots, etc.).

2. WEIGHT. A classification of fabrics with respect to their use is commonly made also on the basis of the weight, which is also a most important factor in establishing the price of a given kind. When a whole piece of the material is available, the weight per yard run or per square yard is readily obtainable. With only a small quantity of the material, the weights of various small pieces of measured areas are determined exactly and the mean taken.

3. COUNT. Yarns are classified according to their count or number, which is the relation between the length and weight of a certain quantity of the yarn and is expressed either as the *length required to give a fixed weight* (not for silk) or as the *weight of a fixed length* (for silk). The count may be determined by means of either the balance or special apparatus.

4. STRENGTH. This is measured by a *dynamometer*, which gives the breaking load or the weight necessary to rupture, under the conditions of the test, a fibre, yarn or strip of fabric of definite dimensions. Usually the dynamometer indicates also the elongation, during the test, of the given length of fibre, yarn or material. Spring, movable weight or lever dynamometers (Perreaux, Moscrop, Schoch, Schopper, Rondet-Schor) are used. Most of the dynamometers work intermittently but some continuously.

5. OTHER TESTS. Various other technical tests are also usually made, e.g. : for yarn, measurement of the torsion and investigation of the uniformity ; for cloth, reduction to tram and organsine, etc.

[1] Giudici : *Tessuti di lana e di cotone* (Milan, 1904) ; P. Heermann : *Mechanisch- und physikalisch-technische Textiluntersuchungen* (Berlin, 1912) ; L. Foux : *Travail des laines à peigne* (Paris, 1913) ; A. Cappelli : *Esame fisico-meccanico delle fibre tessili, filati e tessuti.*

PLATE VI.
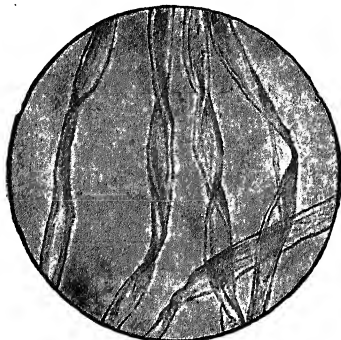
FIG. 68.—Cotton fibres.
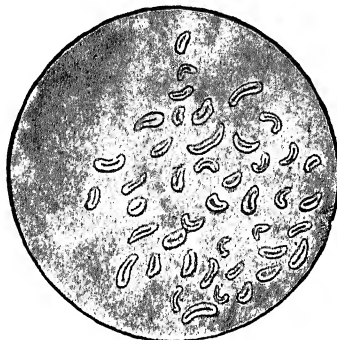
FIG. 69.—Sections of Cotton fibres.
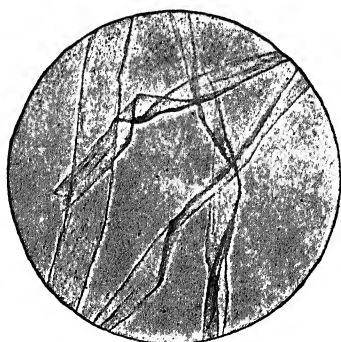
FIG. 70.—Dead Cotton.
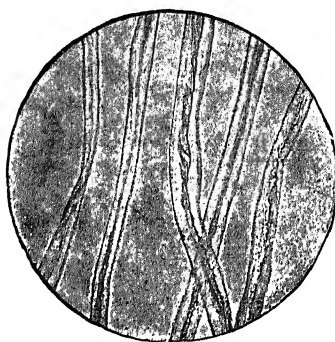
FIG. 71.—Mercerised Cotton.
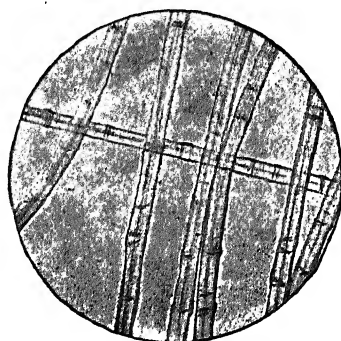
FIG. 72.—Flax.
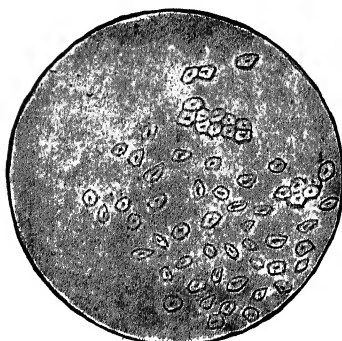
FIG. 73.—Sections of Flax fibres.

PLATE VII.
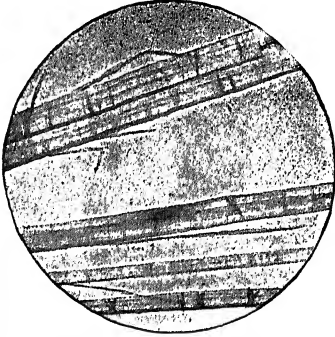
FIG. 74.—Hemp.

FIG. 75.—Sections of Hemp.
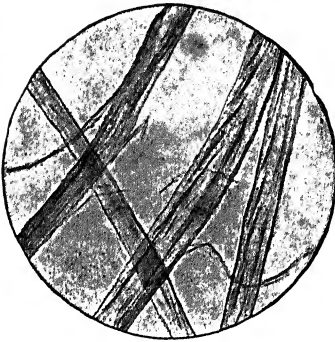
FIG. 76.—Ramie.
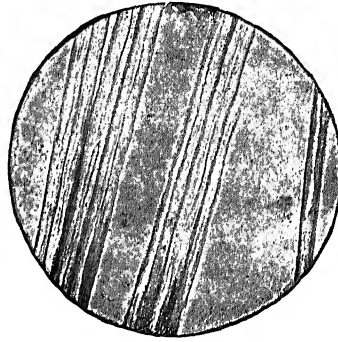
FIG. 77.—Jute.
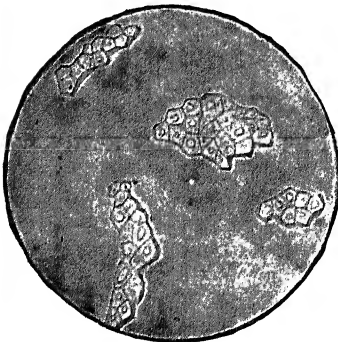
FIG. 78.—Sections of Jute.

FIG. 79.—Agave.

PLATE VIII.
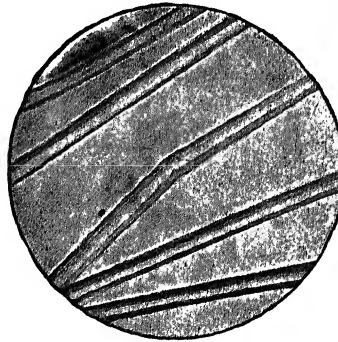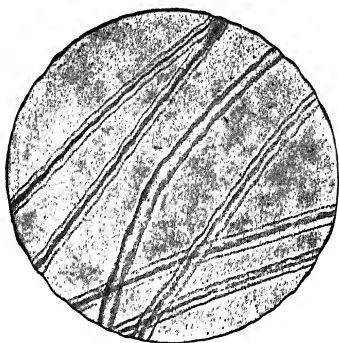
FIG. 80.—New Zealand Flax.
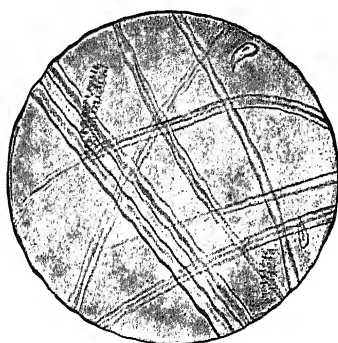
FIG. 81.—Esparto.
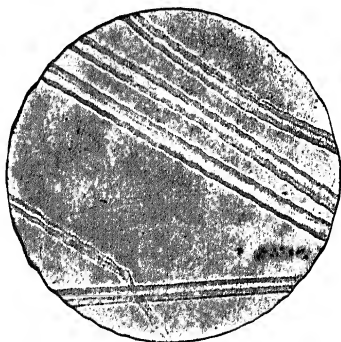
FIG. 82.—Manila Hemp.
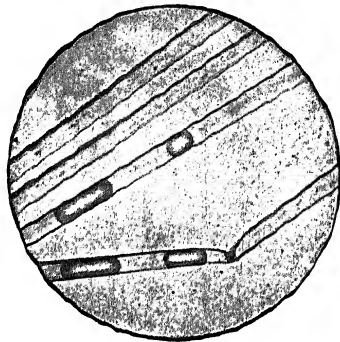
FIG. 83.—Kapok.
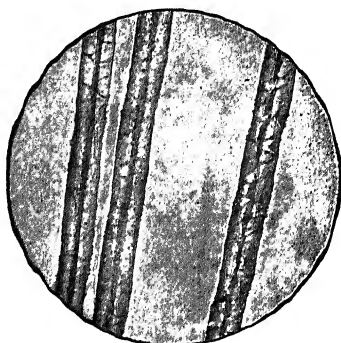
FIG. 84.—Wool with Medulla.

FIG. 85.—Sheep's Wool.

PLATE IX.
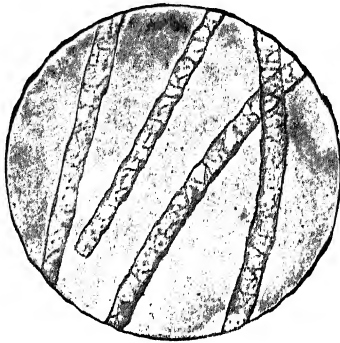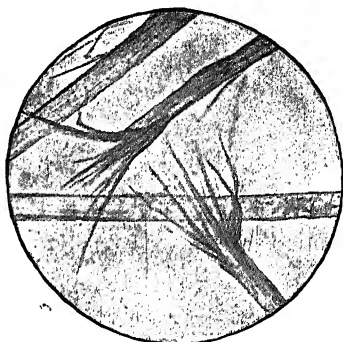
FIG. 86.—Shoddy.
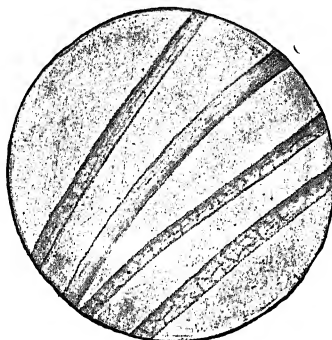
FIG. 87.—Angora wool.
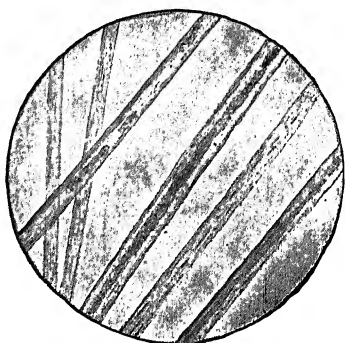
FIG. 88.—Camel's wool.
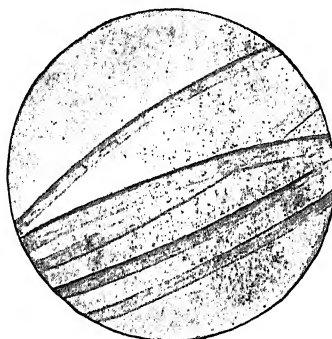
FIG. 89.—Vicuna wool.
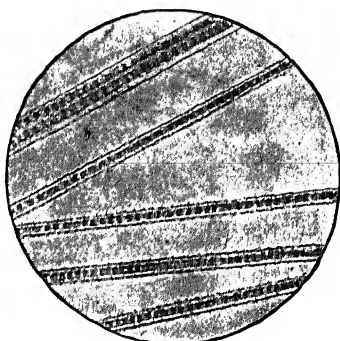
FIG. 90.—Rabbit's fur.

FIG. 91.—Woman's hair.

PLATE X.
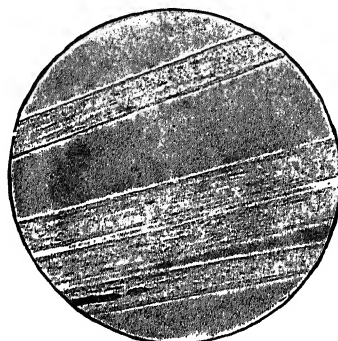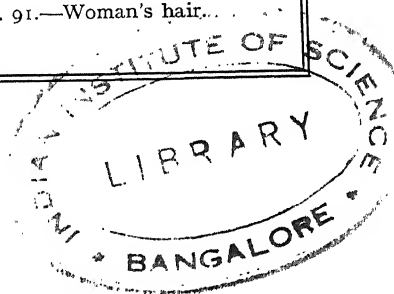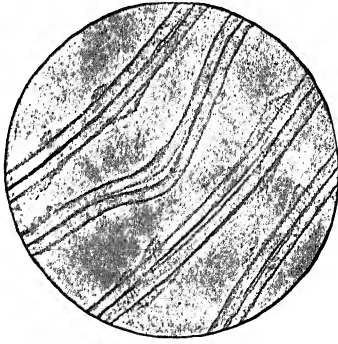
FIG. 92.—Raw Silk.
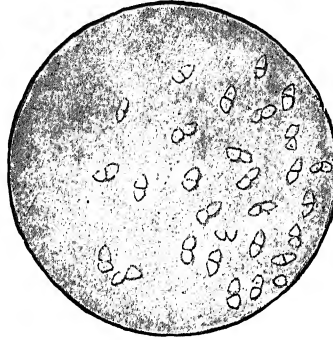
FIG. 93.—Sections of raw Silk.
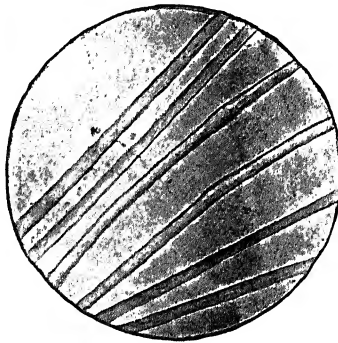
FIG. 94.—Boiled Silk.
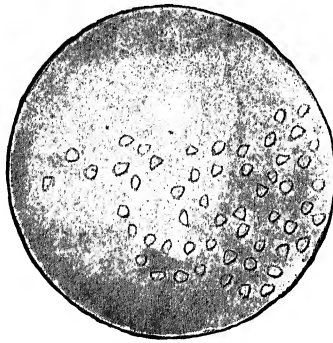
FIG. 95.—Sections of boiled Silk.
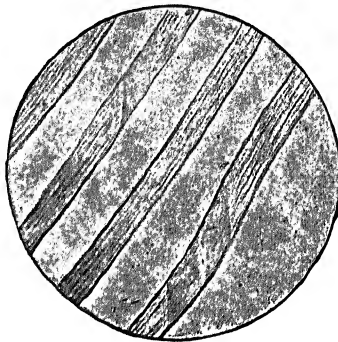
FIG. 96.—Wild (Tussah) Silk.

FIG. 97.—Sections of wild Silk.

PLATE XI.
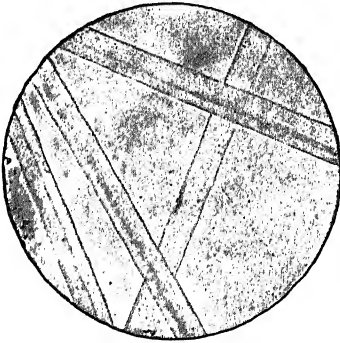
FIG. 98.—Chardonnet Silk.
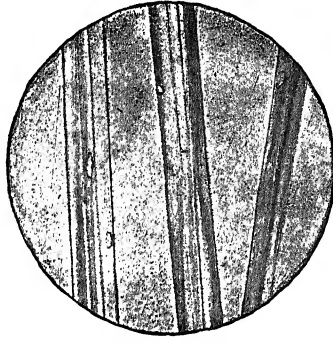
FIG. 99.—Lehner Silk.

FIG. 100.—Sections of Lehner Silk.
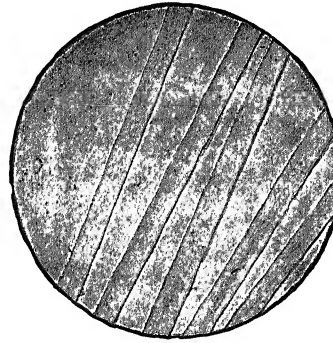
FIG. 101.—Cellulose (Bronnert) Silk.
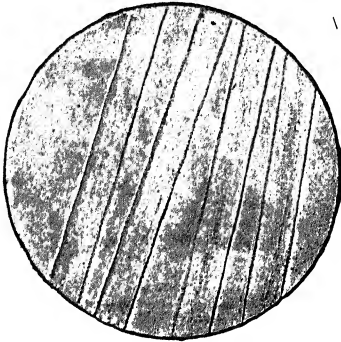
FIG. 102.—Viscose Silk.
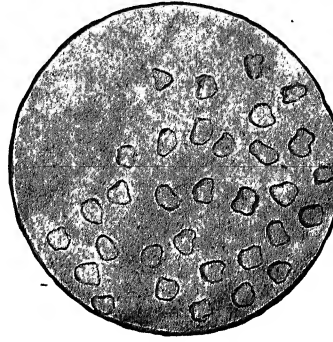
FIG. 103.—Sections of viscose Silk.

INDEX TO VOLUMES I AND II

INDEX

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METHODS AND STANDARDS
for the Chemical Analysis of the Principal
Industrial and Food Products

By

PROFESSOR VITTORIO VILLAVECCHIA

Director of the Chemical Laboratories of the Italian Customs

WITH THE COLLABORATION OF

G. FABRIS	A. BIANCHI	G. ARMANI
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TRANSLATED BY

THOMAS H. POPE, B.Sc., A.C.G.I., F.I.C.

University of Birmingham

VOL. II.

WITH 105 ILLUSTRATIONS IN THE TEXT

TRANSLATOR'S NOTE

In the preparation of the present translation, the points on which it has been considered desirable to depart from the sense of the Italian text are few and mostly unimportant. Notification is made where any appreciable addition to or modification of the original has been made to bring it into conformity with the conditions in this country.

Temperatures are always expressed in degrees Centigrade, and concentrations of aqueous alcohol solutions, according to the French custom, in percentages by volume.

THOMAS H. POPE.

Birmingham.

CONTENTS